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CHANGE OF PHASE UNDER PRESSURE.

II. New Melting Curves With a General Thermodynamic Discussion of Melting.

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Introduction.

In the first paper of this series[1] data were given for the melting under pressure of eleven substances, four of which were found to have new polymorphic forms. The problems offered by polymorphic forms are of great interest and importance; since the writing of the first paper a number of substances have been investigated in this regard, and a number of new forms have been found. This question of polymorphism will be treated in future papers of this series. In the search for new forms a number of substances were investigated without result, whose melting curves lay within the temperature range of this work (0°–200°). These new melting curves are presented in this paper. Complete data are given for nine more substances, and fragmentary data for a few others. In addition, the melting curves of two other substances have been determined, but as these have more than one solid form, the data for them will be reserved for a future paper.

The discussion of melting given in the first paper was almost entirely concerned with the general character of the curve; as to whether it ends

1. P. W. Bridgman, Phys. Rev., N. S., Vol. 3, 126–203, 1914.

* Article to be concluded in next issue.

in a critical point, passes through a maximum temperature, or continues rising indefinitely. The data of the first paper seemed to point conclusively to only one conclusion, namely that within the range of at present realizable pressures there is nothing to indicate that the curve does not rise indefinitely. The data of this paper also all point to the same conclusion; the decreasing curvature of the melting curve and the convexity of the ΔV curve toward the pressure axis are shown by these substances also. The other two new substances with polymorphic forms show the same thing. Fig. 24, at the end of the paper, shows in a striking way that the shape of the melting curve is such that there cannot be a maximum temperature, as Tammann has supposed. In this diagram the slope of the melting curve is plotted against temperature. If there were a maximum, the curves would cross the temperature axis vertically. The direction of curvature shows that this cannot be the case at any temperature, no matter how high, unless there is a reversal of direction of curvature beyond the range of pressures at present realizable. If there is a maximum, these curves should be concave, instead of convex, toward the temperature axis. Up to the present, therefore, we have data on twenty two liquids, to four times the pressure range of previous measurements, all indicating the same answer to the question in hand, without exception. I shall, therefore, in future discussion consider this question as settled. It does not seem worth while to gather any more experimental evidence with this point only in view.

Besides the question as to the ultimate course of the melting curve, other questions are presented by the phenomena of melting. One question of interest is how the course of the melting curve is determined by the separate thermodynamic properties of solid and liquid. As is well known, this problem may be readily solved by the use of the thermodynamic potential. It appears that the thermodynamic quantities which determine the course of the melting curve are the differences of compressibility, thermal expansion, and specific heat (C_p) between solid and liquid. We cannot in general determine all three of these quantities from the data already given for the melting curves, but if one of them can be determined in some other way, there are relations which determine the other two. In some cases, at atmospheric pressure, the data are at hand from which all three of these quantities may be determined. Furthermore, at high pressures, it is shown that certain inequalities hold, in virtue of which we are able to make an estimate of the difference of compressibility between solid and liquid which is correct to perhaps 30 per cent. These very rough values for the difference of compressibility are given and discussed.

There are also now at hand data sufficient to allow the comparison of substances of chemically similar constitution; for instance, CCl_4 with $SiCl_4$, or $CHCl_5$ and $CHBr_5$. Some attention is given to the question as to whether the melting curves show any regularly varying behavior with chemical substitutions of this nature.

It must be recognized, however, that any purely thermodynamic discussion cannot carry us very far on our way. What we are searching for ultimately is a description of the construction of the atom so detailed that we can describe how the atoms are put together in a crystal, and how and why they fall apart when they melt. We are very far indeed from such a goal.

The apparatus was the same as that used in the first paper, and the methods of computation are similar. The tables are somewhat fuller, the values of $d\tau/dp$ being included, and the values of the melting temperatures have been smoothed so as to give differences regular to tenths of a degree. In the preceding paper the equilibrium temperatures were read directly from the curves without further smoothing, so there were irregularities in some cases of several tenths of a degree. These irregularities did not affect the values of $d\tau/dp$, however, which were determined and smoothed in another way. The values of ΔV, $d\tau/dp$, and ΔH given in the tables may not always be exactly related by the thermodynamic equations; this is because these three quantities were smoothed independently, after the calculations had been made. Any such discrepancy, however, is always much less than the probable error with which any of these quantities may be determined.

The data for the individual substances follow.

Detailed Data for Nine Substances.

Bromoform.—Specimens of bromoform from two different sources were used. The first was from Eimer and Amend. It was purified by fractional distillation and crystallization at 0°. There was initially some slight amount of volatile impurity present as shown by the fact that boiling began at 60°, but the boiling point very rapidly rose to 148° and remained there while four fifths distilled. The recrystallized substance was slightly yellow, but had a nearly constant melting point at 7.78°. Five points were determined with this sample, between 900 and 7,000 kgm. This sample was lost by an accident to unrelated parts of the apparatus, when only two more points were necessary for the completion of the curve at high pressures. A fresh lot was ordered from Eimer and Amend, but although this was purified by exactly the same process as the first, the impurity remaining was too large for satisfactory results. An-

other lot was then obtained from the J. T. Baker Chemical Co., made especially to order. This was further purified by the process above, but could not be obtained as pure as the first lot. It melted over a temperature range 0.4° wide, the maximum melting point being 7.62°. The

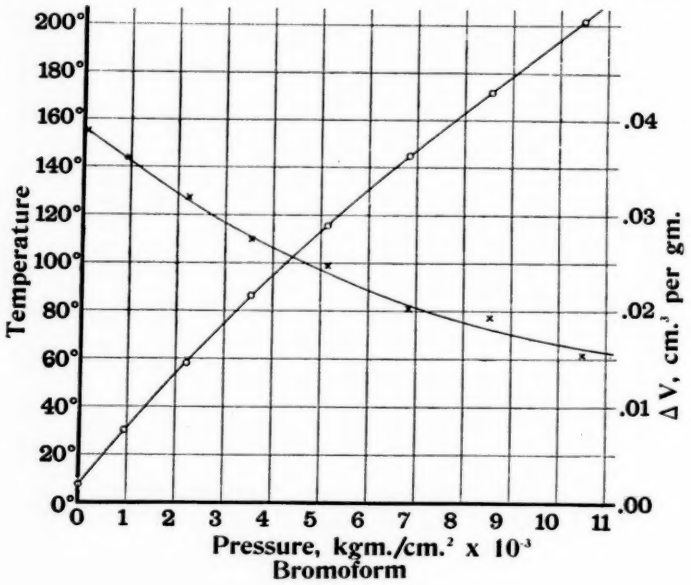

Fig. 1.

Bromoform. The freezing curve and the change of volume curve. The circles show the observed freezing temperatures, and the crosses the observed changes of volume.

corners of the melting curve were, therefore, somewhat rounded, but not so much as to prevent satisfactory results. The points at nearly atmospheric pressure and the two highest pressure points were determined with this sample. From 40 to 44 gm. were used.

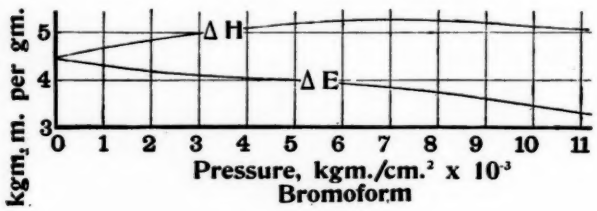

Fig. 2.

Bromoform. The computed values for the latent heat and the change of internal energy when the solid melts to the liquid.

The second set of measurements was made at an interval nearly six months after the first, with a different manganin coil. The $p - t$ points of the second set fit in smoothly with those of the first set, and the

ΔV points of the two sets are consistent within the limits of error, which are here somewhat larger for ΔV than usual. The experimental results are shown in Fig. 1, the computed values of ΔH and ΔE in Fig. 2, and a summary of the numerical values in Table I.

TABLE I.

Bromoform.

Pressure.	Temperature.	ΔV Cm.³/Gm.	$\frac{dT}{dp}$	Latent Heat Kgm. M./Gm.	Change of Energy Kgm. M./Gm.
	°				
1	7.78	0.03906	.0245	4.477	4.477
1,000	31.5	355	230	4.699	4.344
2,000	53.8	322	217	4.852	4.208
3,000	74.9	292	204	4.982	4.106
4,000	94.7	266	192	5.097	4.033
5,000	113.3	243	180	5.217	4.002
6,000	130.8	221	170	5.252	3.926
7,000	147.3	203	162	5.267	3.846
8,000	163.2	188	1565	5.242	3.738
9,000	178.7	176	1535	5.151	3.576
10,000	194.0	166	1515	5.118	3.458
11,000	209.1	157	1500	5.047	3.320

There are several other determinations of the melting point at atmospheric pressure. The earliest is by Thorpe,[2] 2.5°, for what must have been a very impure specimen. Later and better determinations are 7.6° by Steudel,[3] 7.8° by Perkin[4] and 7.5° by Feist and Garnier.[5] The highest of these values, that by Perkin, is in essential agreement with that found above. Perkin remarks at some length on the difficulty of obtaining pure bromoform. He says that it decomposes somewhat on distillation, and that the best method of purification is by repeated crystallization. The density of liquid bromoform is given by Thorpe as 2.8341 at 0° and 2.81165 at 8.56°; by Perkin as 2.90246 for D_{15}^{15} and 2.88253 for D_{25}^{25}, and 2.895 by Feist and Garnier. There seem to be no determinations of the latent heat or the crystalline form.

At room temperature and at 200° no new forms were found between the melting curve and 12,000 kgm. It has been shown by Wahl,[6] however, that at atmospheric pressure there is another modification at low temperature. The reaction to the new form runs only in a narrow interval; the ordinary form may be readily subcooled into a region where

2. T. E. Thorpe, Jour. Chem. Soc., Vol. 37, 141–225, 1880.
3. V. Steudel, Wied. Ann., *16*, 369–394, 1882.
4. W. H. Perkin, Jour. Chem. Soc., Vol. 45, 421–580, 1884.
5. K. Feist und Ch. Garnier, Arch. Pharm., *249*, 458–463.
6. W. Wahl, Proc. Roy. Soc., Vol. 89, 331, 1913.

the reaction to the new form does not run. At high pressures the viscous resistance to the reaction increases, and this may be the reason for my failure to find the new form. However, Wahl does not state the temper-

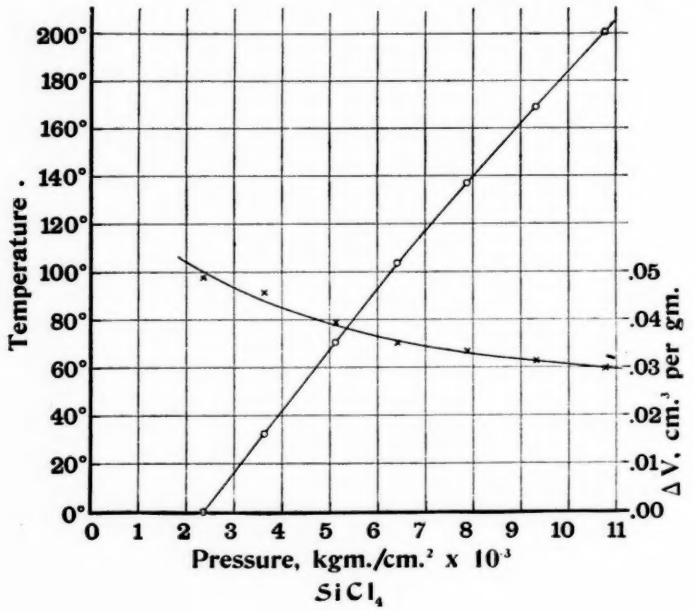

Fig. 3.

Silicon tetrachloride. The freezing curve and the change of volume curve. The circles show the observed freezing temperatures, and the crosses the observed changes of volume.

ature of the transition, and as we have no idea whatever as to the magnitude of the change of volume or the latent heat, one cannot tell whether

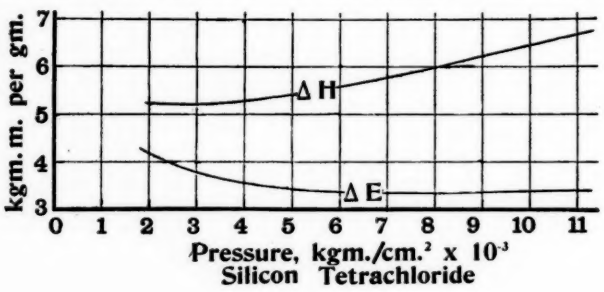

Fig. 4.

Silicon tetrachloride. The computed values for the latent heat and the change of internal energy when the solid melts to the liquid.

any part of the region investigated above contains the region of stability of the new form.

Silicon Tetrachloride.—Measurements were made on only one sample of

$SiCl_4$. This was Kahlbaum's; it is supplied in sealed glass tubes, and was perfectly colorless. No attempt was made to further purify it, as this would require considerable chemical skill, because of its spontaneous decomposition on contact with moist air. The freezing was, nevertheless, gratifyingly sharp, much sharper than appeared likely with a substance of this nature. 21 g. were used.

The experimental results are shown in the curves of Fig. 3, the computed values of ΔH and ΔE in Fig. 4, and the numerical values in Table II.

TABLE II.

Silicon Tetrachloride.

Pressure.	Temperature.	ΔV Cm.³/Gm.	$\frac{dT}{dp}$	Latent Heat Kgm. M. Gm.	Change of Energy Kgm. M./Gm.
	°				
2,000	−10.0	.0522	.0273	5.23	4.19
3,000	+16.7	470	263	5.20	3.79
4,000	42.6	428	256	5.28	3.57
5,000	67.9	395	2485	5.42	3.44
6,000	92.5	368	241	5.56	3.35
7,000	116.3	347	234	5.78	3.35
8,000	139.4	330	228	5.97	3.33
9,000	161.8	317	222	6.23	3.38
10,000	183.8	306	217	6.44	3.38
11,000	205.4	297	213	6.67	3.41

Apparently very few measurements have been made on this substance I have found only one value for the melting point, − 89°, quoted in Kaye and Laby's tables from a source not mentioned. But this value must have been obtained from a very impure specimen, because it lies considerably below any value that the curve above would extrapolate to. It has seemed best, therefore, in Fig. 3 not to try to run the melting curve below 2000 kgm. An unforced extrapolation of the melting curve would give − 67° for the melting point at atmospheric pressure. It would probably be safe to accept this, in lack of other experiments, as a better value than − 89°.

No other modifications of the solid were found to 12,500 kgm. at 30° and to 12,400 kgm. at 200°. This was a disappointment, as I had expected other modifications in analogy with CCl_4; in fact this was the only reason for undertaking the investigation of this substance.

Monochlorbenzol.—This was Kahlbaum's purest, further purified immediately before use. The middle third of the distillate obtained with a Hempel fractionating column proved to be sufficiently pure. Seven points on the melting curve were obtained with this substance, all with the same filling of the apparatus. That the purity was sufficient, is

shown by the ΔV points, which are fully as regular, if not more so, than usual. 17 gm. were used.

The experimental results are shown in Fig. 5, the computed values of ΔH and ΔE in Fig. 6, and the numerical values in Table III.

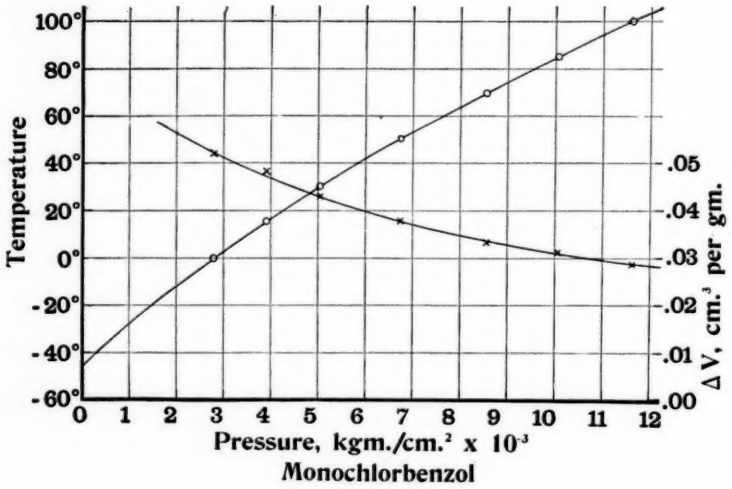

Fig. 5.

Monochlorbenzol. The freezing curve and the change of volume curve. The circles show the observed freezing temperatures, and the crosses the observed changes of volume.

Very recently, in fact since the measurements above were made, the melting point of CH_5Cl has been determined with particular care at atmospheric pressure by Henning,[7] for use as a fixed point in low temper-

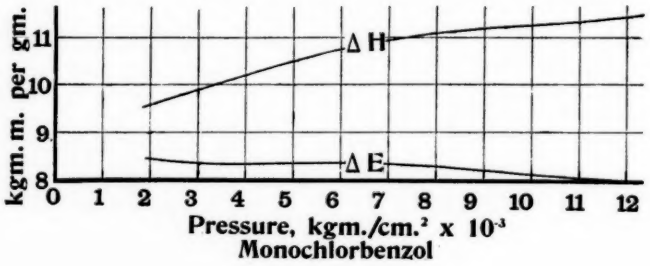

Fig. 6.

Monochlorbenzol. The computed values of the latent heat and the change of internal energy when the solid melts to the liquid.

ature thermometry. His value is $-45.5°$. This lies very well on the curve passing through the points found above at high pressures. Previous values of the melting point were $-40°$, given by Béhal and Valeur,

7. F. Henning, Ann. Phys., Vol. 43, 282–294, 1914.

TABLE III.

Monochlorbenzol.

Pressure.	Temperature.	ΔV Cm.^{3}/Gm.	$\frac{d\tau}{dp}$	Latent Heat Kgm. M./Gm.	Change of Energy Kgm. M./Gm.
1	−45.5°		.0184		
1,000	−28.0		167		
2,000	−12.0	.0565	154	9.58	8.45
3,000	+ 2.9	511	1425	9.90	8.36
4,000	16.7	469	133	10.22	8.34
5,000	29.7	432	125	10.47	8.31
6,000	41.9	400	117	10.76	8.36
7,000	53.3	372	111	10.93	8.33
8,000	64.0	349	106	11.10	8.31
9,000	74.4	328	102	11.18	8.23
10,000	84.5	311	099	11.24	8.13
11,000	94.2	297	0965	11.31	8.04
12,000	103.6	285	094	11.42	8.00

− 45° by Schneider,[8] and − 44.9° by Haase.[9] These figures are interesting, because without other evidence one is always inclined to accept the highest listed value of a melting point as most probably accurate.

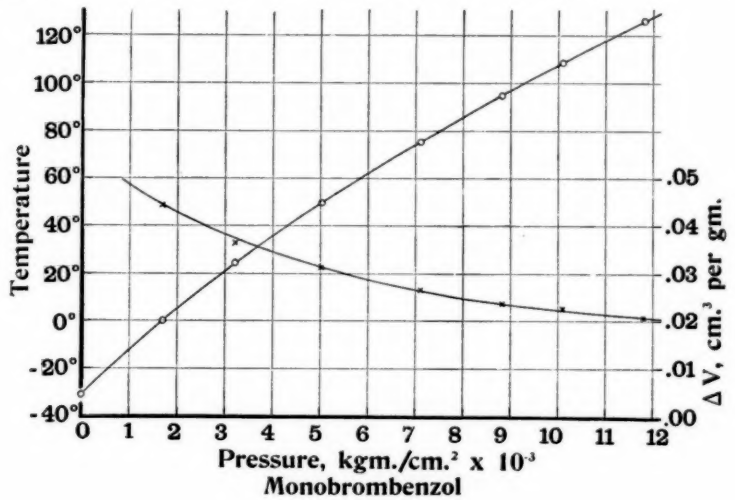

Fig. 7.

Monobrombenzol. The freezing curve and the change of volume curve. The circles show the observed freezing temperatures, and the crosses the observed changes of volume.

lower values being explained by impurities, whereas here, the more recent and more accurate values are lower. For the density we have by

8. B. V. Schneider, ZS. phys. Chem., *22*, 225–240, 1897.

9. E. Haase, Ber. D. Chem. Ges., *26*, 1052–1054, 1893.

Adrieenz[10] 1.1284 at 0° and 1.1052 at 21.69°, and by Biron[11] 1.1279 at 0° and 1.1064 at 20°. There seem to be no determinations of the latent heat or the change of volume at atmospheric pressure or of the crystalline form. An extrapolation of the above values for ΔV, assuming constant second differences, gives 0.0711 cm.³/gm. Corresponding to this is the value 8.77 kgm.m./gm. or 19.7 cal./gm. for the latent heat.

At 30° and at 100° no new modification of the solid was found to 12,800

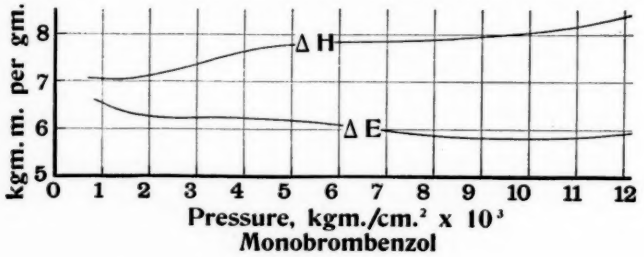

Fig. 8.

Monobrombenzol. The computed values of the latent heat and the change of internal energy when the solid melts to the liquid.

kgm. From analogy with benzol, it would not have been surprising if there had been a second form.

Monobrombenzol.—Like monochlorbenzol, this was Kahlbaum's purest, and was further purified by fractional distillation. The purity is sufficient as evidenced by the regularity of the points. Seven points were obtained, all with the same filling of the apparatus. 23 gm. were used.

TABLE IV.

Monobrombenzol.

Pressure.	Temperature.	ΔV Cm.³/Gm.	$\frac{d\tau}{dp}$	Latent Heat Kgm. M./Gm.	Change of Energy Kgm. M./Gm.
1	−31.1		0.0197		
1,000	−12.1	0.0486	181	7.010	6.524
2,000	5.3	428	167	7.134	6.278
3,000	21.3	382	1525	7.375	6.229
4,000	35.9	345	140	7.615	6.235
5,000	49.4	315	131	7.756	6.181
6,000	62.0	288	123	7.845	6.117
7,000	74.1	266	118	7.827	5.965
8,000	85.7	248	114	7.868	5.868
9,000	96.9	234	109	7.943	5.837
10,000	107.6	222	105	8.050	5.830
11,000	117.9	212	102	8.127	5.795
12,000	127.9	205	098	8.389	5.929

10. A. Adrieenz, Ber. D. Chem. Ges., *6*, 441–444, 1873.

11. E. Biron, Jour. russ. phys. Chem. Ges., *42*, 135–166.

The experimental results are shown in Fig. 7, the computed values of ΔH and ΔE in Fig. 8, and the numerical values in Table IV.

For the melting point at atmospheric pressure we have $-30.5°$ by Schneider,[8] $-30.7°$ by Bugarsky,[12] and $-31.3°$ by Haase.[9] Here, as in the case of chlorbenzol, the lower value, $-31.3°$, seems to be probably more accurate, since the curve extrapolates to this without any initial abnormalities in $d\tau/dp$. For the density of the liquid Biron[11] gives 1.5223 at 0° and 1.4953 at 20°, Adrieenz[10] 1.5177 at 0° and 1.4898 at 20.96°, and Wagner[13] 1.5203 at 0° and 1.4945 at 20°. There seem to be no values of change of volume or of latent heat for comparison at atmospheric pressure. We may extrapolate from the values of Table IV. and find at atmospheric pressure 0.0564 cm.^{3}/gm. for the change of volume, and 7.0 kgm. m./gm. for the latent heat. There are apparently no other measurements for comparison at high pressures. The crystalline form has not been determined.

At 25°, no new modification of the solid was found to 12,500 kgm., and at 126°, no new form to 12,700 kgm.

Benzophenone.—This substance was obtained from Eimer and Amend, and was further purified by crystallization at constant temperature in the thermostat. The temperature was so adjusted that crystallization took place very slowly, during 48 hours. Large perfect crystals were obtained. 13 to 18 gm. were used.

Various accidents made necessary measurements at four different times with four different fillings of the apparatus. The benzophenone was placed in an inverted nickel steel shell, instead of the bulb used for substances liquid at room temperature. This shell will be further described in the next paper dealing with solids. With the first filling of the apparatus a complete series of measurements was made over the entire pressure range, but on taking the apparatus apart it was found that the shell had split at some time during the application of pressure, allowing some of the benzophenone to escape. On working up the results, an abrupt drop in the values of ΔV showed that the precise point at which this had taken place was after the determination of the first point. The splitting of the nickel steel shell seems to have been caused by a quite unusual rigidity of this substance under pressure. Of course the values of pressure and temperature found during this first run were quite unaffected by the escape of some of the material; it was the ΔV values that had to be discarded, only the first being good. The second filling was made for a determination of the point at nearly atmospheric pressure;

12. Bugarsky, Math. u. Naturw. Ber. aus Ungarn, *26*, 89–151, 1910.
13. F. Wagner, Lieb. Ann., *221*, 61–107, 1883.

this was accomplished without incident and with unusually sharp freezing. The third filling of the apparatus gave three points with good values of ΔV at 1,200, 3,200 and 2,200 kgm. This set of readings was terminated by the breaking of the lower cylinder into two cleanly divided halves, a rather unusual fracture. Apparently it had been started by an explosion some time previously. The fourth set of readings gave the two points needed to complete the curve at the highest pressures. The data given

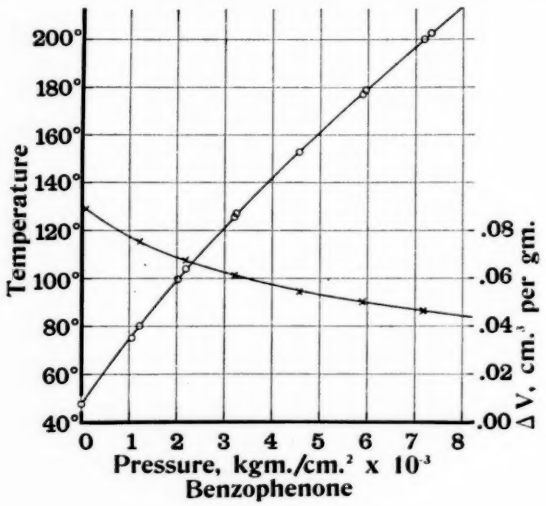

Fig. 9.

Benzophenone. The freezing curve and the change of volume curve. The circles show the observed freezing temperatures, and the crosses the observed changes of volume.

amount, then, to a double determination of the coördinates of the melting curve, and a single determination of the course of the ΔV curve, but with four different fillings of the apparatus, with different quantities of material.

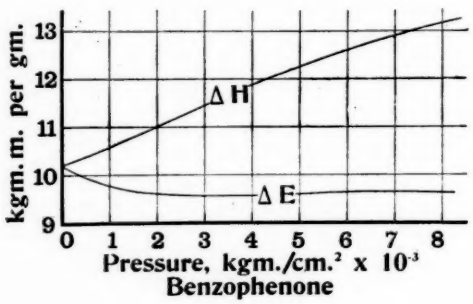

Fig. 10.

Benzophenone. The computed values of the latent heat and the change of internal energy when the solid melts to the liquid.

The experimental results are given in Fig. 9, the computed values of ΔH and ΔE in Fig. 10, and the numerical values in Table V.

TABLE V.

Benzophenone.

Pressure.	Temperature.	ΔV Cm.³/Gm.	$\frac{d\tau}{dp}$	Latent Heat Kgm. M./Gm.	Change of Energy Kgm. M./Gm.
	°				
1	47.77	0.0904	.02845	10.20	10.20
1,000	74.6	773	2545	10.56	9.79
2,000	98.9	689	2330	11.00	9.62
3,000	121.3	624	2145	11.48	9.61
4,000	142.0	571	2000	11.85	9.57
5,000	161.3	532	1885	12.26	9.60
6,000	179.6	498	1785	12.63	9.64
7,000	197.0	468	1705	12.90	9.62
8,000	213.7	442	1635	13.17	9.63

There are a number of values for comparison. For the melting point, Tammann[14] gives 48.11° in Kristallisieren und Schmelzen, 47.7° in 1898, and 48.5° in 1899. Linnemann[15] gives 48° to 48.5°, Bruner[16] 48.0°, Hulett[17] 48.10°, and Block[18] 48.1°. The value found directly for the sample above, 47.77°, is evidently too low; the best value selected from the above is probably about 48.11°. For the change of volume Tammann[19] gives 0.0875 to 0.0883 cm.³/gm., and Block[18] 0.0877 against 0.0904 above. For the latent heat, Tammann[19] gives 23.4 from a direct determination and 23.95 cal. calculated from the coördinates of the melting curve. Eykmann[20] determines it as 23.2 from the depression of the freezing point, and Bruner[16] gives the value 23.7. The value that I found above was 23.9; the agreement of all these values is closer than usual. The melting curve found by Tammann at high pressures lies somewhat below that given above, the discrepancy increasing as usual with increasing pressure, but the difference is somewhat less than usual. At 90° my pressure is 20 kgm. lower than his; at 100°, 60 kgm. lower; and at 130°, 160 kgm. lower. Tammann's values for ΔV also drop off with increasing pressure more rapidly than do mine, but the discrepancy is not so much as for many other substances. In addition to Tammann, Hulett[17] has also

14. G. Tammann, "K. und S.," p. 229. Wied. Ann. *66*, 491, 1898. ZS. phys. Chem., *29*, 51–76, 1899.

15. Ed. Linnemann, Lieb. Ann., *133*, 1–32, 1865.

16. L. Bruner, ZS. Chem., *4*, 497–519, 1899.

17. G. H. Hulett, ZS. phys. Chem., *28*, 629–672, 1899.

18. H. Block, ZS. phys. Chem., *78*, 385–425, 1912.

19. G. Tammann, "K. und S.," p. 231.

20. J. F. Eykmann, ZS. phys. Chem., *4*, 497–519, 1889.

determined the effect of pressure on the melting point up to 300 kgm. His values agree with mine better than with Tammann's. Thus for the initial slope, $d\tau/dp$, Tammann gives 0.0276, Hulett 0.0289, and I find 0.02845.

At 30°, I found no new modification to 12,000 kgm., and at 200° none to 12,500. This result is an interesting one in view of the well known tendency of benzophenone to crystallize in other forms at atmospheric pressure. At least three other, unstable, forms are known at atmospheric pressure. The existence of these unstable forms seems connected in some way with the rather unusual amount of subcooling that benzophenone will allow. If it is allowed to crystallize from the subcooled condition it is likely that an unstable form will appear, rather than the normal stable form. Now in these experiments at high pressures, in which freezing was produced by increasing pressure at constant temperature, it was often necessary to push the pressure considerably beyond the equilibrium value, that is, to produce considerable subcooling, before crystallization could be induced. Yet never did any other than the normal crystal appear, although analogy with the behavior at atmospheric pressure would lead one to expect the sporadic occurrence of unstable forms. The amount of superpressure necessary to produce solidification varied capriciously, as is to be expected, and might be rather large. Once, at 179°, 450 kgm. superpressure was necessary, at 80°, 1,500 kgm., and again at 177°, 2,600 kgm. These values correspond to 9°, 34°, and 46° subcooling. No serious effort was made to obtain regular values for the subcooling; doubtless better values could be found, but there must always be an element of caprice about anything of this kind.

There may be two reasons for the failure ever to observe any of the unstable forms. Tammann has noticed that the unstable forms are much more difficult to produce and that they change spontaneously to the stable form much more readily when there is a metal in contact with the benzophenone than when only glass is used. For these experiments contact with some metal, mercury to transmit the pressure if nothing else, is unavoidable, so that the conditions are never favorable to the appearance of unstable forms. In the second place, there may of course be a specific temperature or pressure effect, the unstable nuclei being less likely to form at the high temperatures. This is not unlikely, and is somewhat borne out by the tendency, in a rough way, for the possible subcooling to become less at high temperatures. At atmospheric pressure, for instance, a subcooling of 100° is possible under the proper conditions. On the whole, then, the chances seem unfavorable for the study of the unstable forms under pressure. No very serious attempt was made to do

this in the present work, but it is significant that F. Körber,[21] one of Tammann's pupils, in a recent investigation of the effect of pressure on unstable forms, has not included benzophenone in his list of substances.

The same sluggishness that is manifested in the large amount of possible subcooling has also made possible a rough qualitative examination of the velocity of crystallization under pressure. This is not possible for most substances, because the heat of reaction is the dominating factor for those substances with a normal rate of crystallization, the crystallization proceeding as fast as the heat of reaction can be conducted away through the walls of the pressure cylinder. A consequence of this is that for most substances the melting when the solid is superheated takes place as rapidly as the freezing when the liquid is subcooled in the presence of the solid. The velocity of these reactions is indicated very simply by the rate at which pressure returns to its equilibrium value after it has been displaced to the one side or the other. But with benzophenone the velocity of crystallization is so slow that the heat of reaction has a chance to be dissipated rapidly enough not to entirely mask the normal progress of the

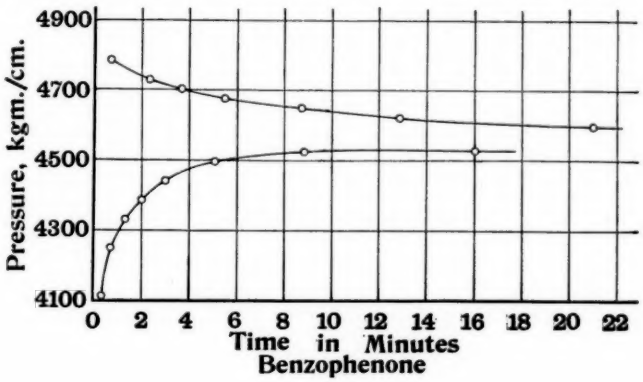

Fig. 11.

Benzophenone at 152°. Shows the recovery of pressure, when pressure has been displaced from the equilibrium value, plotted against time. On the rising curve, the solid is melting, and on the falling curve the liquid is crystallizing. Note that the rate of melting is more rapid than that of crystallization. In the actual experiment, the melting curve was obtained first; in the diagram the freezing curve has been displaced in time for convenience of comparison.

reaction. It has been possible to establish the fact for benzophenone that the velocity of crystallization is very much less than that of melting. Careful measurements were made of the rate of spontaneous recovery of pressure from above and below at five different temperatures. Figure 11 reproduces one of these curves for the reaction velocity from above and below. The greater speed of melting is shown by the sharper corner

21. F. Körber, ZS. phys. Chem., *82*, 45–55, 1913.

of the curve. An examination of all five curves shows that the velocity of melting does not vary markedly with temperature, indicating no large variation in thermal conductivity with rising temperature and pressure along the melting curve. But it does seem probable, although it is not entirely certain, that the velocity of crystallization increases with rising temperature. Because of the impossibility of superheating a solid, the velocity of melting will, of course, always be determined essentially by the heat conductivity of the walls. Irregularity in measurements of this kind is to be expected. For example, if it happened that at higher temperature the crystallization grew from one chance nucleus, while at low temperatures there were two, then the rate of recovery at low temperatures might be greater, although the actual velocity of crystallization

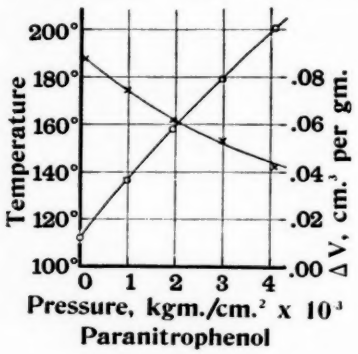

Fig. 12.

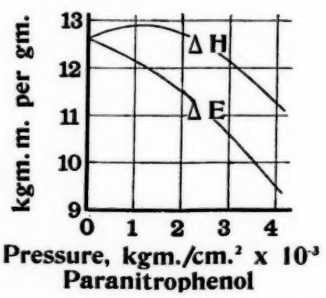

Fig. 13.

Paranitrophenol. The freezing curve and the change of volume curve. The circles show the observed freezing temperatures, and the crosses the observed changes of volume.

Paranitrophenol. The computed values of the latent heat, and the change of internal energy when the solid melts to the liquid.

might be less. The question of reaction velocity will be considered at greater length in a future paper of this series.

Paranitrophenol.—Merck's " blue label " preparation was used without attempt at further purification. There was considerable impurity present as shown by the low value of the freezing point and the rounding of the corners of the melting curve. In fact, this is one of the most impure of the substances for which data are given here. Error from the rounding of the corners of the melting curves was largely avoided, however, by running the pressure an unusual distance beyond the freezing point, allowing a better extrapolation.

Two sets of measurements were made; one comprised points at four pressures above 900 kgm., and the other was the usual measurement with the low pressure apparatus at approximately atmospheric pressure. The quantities used were 15.7 and 20.0 gm. respectively.

The observed points are shown in Fig. 12, the computed values of ΔH and ΔE in Fig. 13, and the numerical values in Table VI.

TABLE VI.

Paranitrophenol.

Pressure.	Temperature.	ΔV Cm.³/Gm.	$\frac{d\tau}{dp}$	Latent Heat Kgm. M./Gm.	Change of Energy Kgm. M./Gm.
	°				
1	112.4	.0891	.02720	12.63	12.63
500	125.5	812	2524	12.82	12.41
1,000	137.7	740	2356	12.90	12.16
1,500	149.1	674	2208	12.89	11.88
2,000	159.8	614	2090	12.72	11.49
2,500	170.0	564	2000	12.49	11.08
3,000	179.8	520	1940	12.14	10.58
3,500	189.4	480	1894	11.71	10.03
4,000	198.8	445	1866	11.26	9.48

The normal melting point of this substance is given as high as 115° by the Chemiker Kalendar, but the authority is not stated. The melting point is given as 114° by Schiff,[22] 114° by Wagner,[23] and 111.46° by Mills.[24] The value found above, by an extrapolation of the value at 80 kgm., was 112.4°. For the density of liquid nitrophenol, Schiff [22] gives the formula $1.2809 - 0.00095\ (t° - 114)$, and for the density of the solid at room temperature Schroeder[25] gives 1.468. Assuming the value found above for ΔV, this gives 0.00015 as the value of the mean dilatation of the solid between room temperature and the melting point. At high pressures there are no previous measurements for comparison.

No new modification of the solid was found to 12,000 kgm. either at room temperature or at 200°. The region between atmospheric pressure and 2,000 kgm. was investigated with rather more than usual care at room temperature. The chief reason for undertaking the investigation of this substance at all is that it is usually listed as one with two modifications at atmospheric pressure; in fact the recent Tables of the Société Française marks this substance with an asterisk as a particulary striking example of a polymorphic transition. The low temperature form is supposed to be a bright pink which changes to a nearly colorless form on warming. This is usually stated on the authority of Lehmann;[26] he is sometimes quoted as saying that this transition is enantiotropic and

22. R. Schiff, Lieb. Ann., *223*, 247–268, 1884.
23. P. Wagner, Ber. D. Chem. Ges., 7, 76–78, 1874.
24. E. J. Mills, Phil. Mag. (5), Vol. *14*, 1–29, 1882.
25. A. Schroeder, Ber. D. Chem. Ges., *12*, 561–567, 1879.
26. O. Lehmann, ZS. Kryst., *1*, 43–48, 1877.

sometimes as monotropic. His original statement is monotropic. In the Tables of the French Society his unstable and stable forms have been interchanged. In an attempt to determine whether there is a transition at low pressures, perhaps unaccompanied by a change of color, dilato-

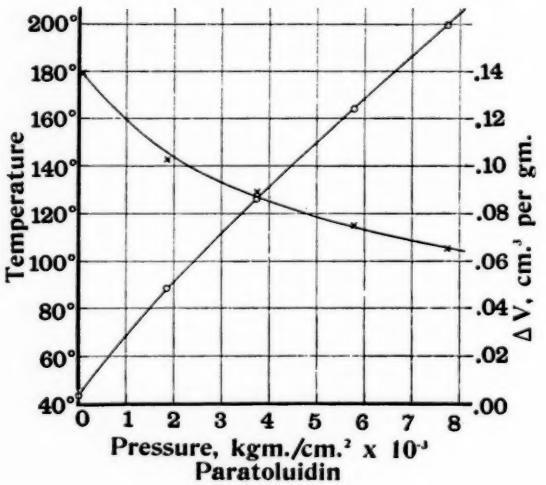

Fig. 14.

Paratoluidin. The freezing curve and the change of volume curve. The circles show the observed freezing temperatures, and the crosses the observed changes of volume.

metric measurements were made in the low pressure apparatus at a constant pressure of 80 kgm. No perceptible volume change could be found between 30° and the melting point.

Paratoluidine.—This substance was obtained from Eimer and Amend,

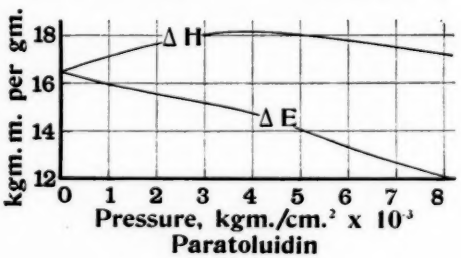

Fig. 15.

Paratoluidin. The computed values of the latent heat and the change of internal energy when the solid melts to the liquid.

and was purified by crystallization at constant temperature in the thermostat. Crystals in the form of needles several inches long were obtained. The impurity shown by the rounding of the corners was, however, somewhat more than usual. To avoid errors from this cause in

the ΔV determinations, measurements were usually begun 1,500 kgm. beyond the melting point. Only two sets of measurements were made; one of four points at high pressures, and one at 80 kgm. In addition, the melting point was determined at atmospheric pressure. The quantities used were 12 and 16 gm.

The experimental results are shown in Fig. 14, the computed values of ΔH and ΔE in Fig. 15, and the numerical values in Table VII. Es-

TABLE VII.

Paratoluidine.

Pressure.	Temperature.	ΔV Cm.^{3}/Gm.	$\frac{d\tau}{dp}$	Latent Heat Kgm. M./Gm.	Change of Energy Kgm. M./Gm.
	°				
1	43.6	.1413	.0271	16.51	16.51
1,000	69.0	.1195	238	17.17	15.97
2,000	91.5	.1037	214	17.66	15.59
3,000	112.0	.0931	1977	18.04	15.25
4,000	131.3	.0852	1894	18.19	14.78
5,000	150.0	.0789	1854	18.01	14.06
6,000	168.4	.0736	1831	17.74	13.32
7,000	186.6	.0688	1810	17.48	12.66
8,000	204.6	.0647	1794	17.22	12.04

pecially noteworthy is the rapid approach to linearity of the melting curve at the higher pressures, and the unusually large volume change at atmospheric pressure.

The melting point at atmospheric pressure of the specimen used above was 43.6°. The Chemiker Kalendar gives 45° for the melting point, but the authority is not cited; probably this is from Brühl.[27] Other values for the melting point are 38.90° by Batteli,[28] 42.89° by Mills,[24] 43.3° by Tammann,[29] 43.73° by Hulett,[17] and 38.7° by Block.[18] The value of Hulett seems to be the best. For the latent heat we have the following values. O. Pettersson[30] gives 37.3 cal. as recomputed by Tammann from Pettersson's value 35.8 at 31° so as to reduce to the melting point. Tammann[29] calculates from his own data 35.6 cal. for the latent heat. Batteli[28] gives 39.3, Eykmann[20] finds 38.6, and I find by calculation from my own data 38.7 cal. For the density Rüdorff[31] gives 1.046 at room temperature, and Brühl[27] 0.9538 for the liquid at 59.1°. For the change of volume, Batteli[28] gives 0.066 cm.^{3}/gm., and Block[18] 0.0877 at atmospheric pressure, against my value 0.1413 above. Tammann[29] gives one

27. J. W. Brühl, ZS. phys. Chem., *16*, 193–225, 1895.
28. A. Batteli, R. Ist. Ven. (6), *3*, 1781–1811, 1884–85.
29. G. Tammann, "K. und S.," p. 240.
30. O. Pettersson, Jour. prak. Chem., *24*, 129–168, 1881.
31. Fr. Rüdorff, Ber. D. Chem. Ges., *12*, 249–252, 1879.

value under pressure, 0.115 at 575 kgm. against 0.1283 above. There must have been some blunder in the values of Batteli and Block, because they would give impossibly low values for the latent heat when combined according to Clapeyron's equation with the values of $d\tau/dp$, in which Tammann, Hulett, and I are in essential agreement. Tammann has determined the coördinates of the melting curve to 3,000 kgm. At 1,000 kgm. his value is 1.3° lower than mine, at 2,000, 2.1° lower, and at 3,000, 3.6° lower. Hulett[17] also measured the effect of pressure on the melting curve up to 300 kgm. His initial value of $d\tau/dp$ is 0.0270 against 0.0271 above.

No new modifications of the solid were found up to 12,000 kgm., either at room temperature or 200°.

Methyl Oxalate.—It is a matter of considerable difficulty to obtain this substance pure, and it was necessary to make several attempts. The first sample was from Eimer and Amend, made especially to my order, and as furnished by them had a melting point of 48°. It was further purified by distilling in air at atmospheric pressure and crystallizing in the thermostat; this raised the melting point to 52.96°. The melting point of the pure substance is listed as 54°. With this sample three points on the melting curve were obtained between 35° and 175°, and also the change of volume at low pressures. There was considerable rounding of the corners of the melting curve, but the results showed conclusively that there was no second modification, a point which will be touched on again later. The series of runs with the first sample was discontinued because of accidental loss of all the purified substance. Another sample, obtained from the ordinary stock of the Harvard Chemical Laboratory, had a melting point of 49°, but no attempt was made to further purify it. A second lot was then obtained from Eimer and Amend, but the same process of purification as that applied to the first sample did not yield a product with so high a melting point. Part of the impurity in these first samples was probably introduced by the process of distillation; it seems certain that some decomposition is caused by heating to 163°, the boiling point at atmospheric pressure. Finally, a special sample was made at the Harvard Chemical Laboratory under the direction of Professor Kohler. The method was not an uncommon one; esterification of pure anhydrous oxalic acid, using pure methyl alcohol and a small quantity of pure sulfuric acid. Especial pains was taken to start with pure reagents; Professor Kohler tells me that it is very difficult to remove the impurities if they have once got into the methyl oxalate, but that one must have purity from the start. This sample came in the form of flakes, which were quite dry and not adherent to each other,

whereas the other samples had been obviously impure with some slight moisture. The great purity of this specimen is shown by its high melting point, 54.14° at atmospheric pressure when half melted, as

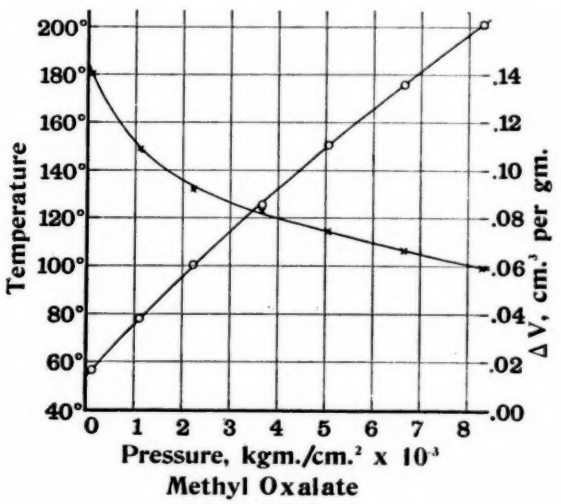

Fig. 16.

Methyl oxalate. The freezing curve and the change of volume curve. The circles show the observed freezing temperatures and the crosses the observed changes of volume.

obtained by extrapolation from the melting point at 100 kgm. This seems to be somewhat higher than any value previously listed. This melting point can be counted on with some certainty, because at 100 kgm.

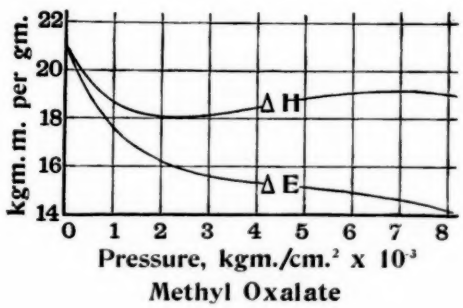

Fig. 17.

Methyl oxalate. The computed values of the latent heat and the change of internal energy when the solid melts to the liquid.

it was possible to shut the equilibrium pressure within two values differing by only 3 kgm., the equivalent of 0.07°, when approached from above and below. There was, nevertheless, some slight impurity in this best sample, because it was possible to detect a slight rounding of the corners. At

80 kgm., where the true melting temperature is 56°, this rounding was perceptible at 50°, but was imperceptible at 45°. In this connection it may pay to emphasize the very delicate criterion of impurity afforded by the rounding of the corners. At 50°, the rounding was such as to amount to a premature melting of 0.0082 of the total quantity. This would mean a total depression of the freezing point, if the impurity were uniformly distributed throughout the mass, of 0.10°. We may, therefore, assume 54.24° as the most probable melting point of the absolutely pure substance at atmospheric pressure. The rounding of the corners became somewhat greater at the high pressure end of the melting curve. Evidently the high temperature caused some decomposition under pressure, just as it does when distillation is attempted at atmospheric pressure. The rounding was not large, however, and should not affect appreciaby the correctness of the values for equilibrium pressure and temperature, and only slightly the values for the change of volume.

Two runs, with two different fillings of the apparatus were made; one for all the points at high pressures, and the other for the one point at low pressure.

The experimental values for equilibrium pressure and temperature and the changes of volume are shown in Fig. 16, the computed values of latent heat and change of internal energy in Fig. 17, and the numerical values are collected in Table VIII. In this table the equilibrium tem-

TABLE VIII.

Methyl Oxalate.

Pressure.	Temperature.	$\Delta l'$ Cm.^{3}/Gm.	$\frac{d\tau}{dp}$	Latent Heat Kgm. M./Gm.	Change of Energy Kgm. M./Gm.
	°				
1	54.24	0.1453	.02261	21.03	21.03
1,000	75.8	.1115	2078	18.71	17.60
2,000	95.8	.0957	1946	18.13	16.22
3,000	114.7	.0862	1838	18.19	15.60
4,000	132.6	.0798	1747	18.52	15.33
5,000	149.6	.0745	1669	18.87	15.14
6,000	165.9	.0696	1601	19.08	14.90
7,000	181.6	.0650	1544	19.14	14.59
8,000	196.8	.0606	1496	19.03	14.18

peratures have been corrected by adding 0.10° to the observed temperatures, this correction being obtained from the data above for the rounding of the corners at 77 kgm., and using the assumption that the depression does not change markedly with pressure. The legitimateness of this assumption has been discussed in the first paper of this series.

The initial rapid decrease of the latent heat is an unusual feature; this accompanies the rapid initial decrease in the change of volume, which may be open to question.

The points obtained with the first impure sample at 135°, 155° and 175°, were all about 5° too low; this is probably to be explained by the escape of some of the methyl oxalate and contamination with the kerosense, as well as by the known initial impurity of the sample. This contamination with kerosene was the accident alluded to above which made necessary the abandonment of this sample; it was not detected until these three points had been measured. The value for the change of volume obtained with the impure substance at low pressure is not affected by the error of the high pressure points, and may be expected to be more nearly correct. This value at 77 kgm. was 0.132 cm.^{3} per gm., which is distinctly lower than that found for the pure sample. This shows the importance of using pure substances if accurate values of the change of volume are expected.

The particular object of working with this substance was that it is one for which Tammann[32] has announced the existence of two modifications. Tammann states that there is a transition point at about 25° at atmospheric pressure; from this point the transition line between the two varieties runs upwards to a triple point at 54.0° and 550 kgm. The domain of existence of Tammann's variety I is, therefore, very restricted in extent. I could find no trace whatever of this supposed second modification. Search was made at 77 kgm. by raising temperature from 13° to the melting point in steps of 5°, and at 40° I could find nothing with increasing pressure to 700 kgm., although Tammann's transition line should be found at 300 kgm. at this temperature. There seems to be little question that this result of Tammann's was due to impurity of his sample, which he states had a melting point from 49.5° to 50.2°. In private correspondence, Professor Tammann has suggested to me that the existence of the second variety may be possible only in the presence of impurity, because cases are known in which an unstable variety is formed only in the presence of impurity. This, however, would demand that Tammann's sample was even more impure than would be indicated by the low value of his melting point. If there really are two modifications, there can be little doubt that the modification of Tammann which is stable over by far the greater portion of his pressure range is identical with the variety which I have measured; that is, Tammann's variety II is the same as that measured above. But Tammann's data would demand that the melting point of II be 46.8° at atmospheric pressure,

32. G. Tammann, "K. und S.," p. 265.

which would mean that his sample contained enough impurity to depress the freezing point by 7.3°. That there is some grave fault with Tammann's measurements on this substance is further indicated by the fact that the coördinates which he gives for the melting curve are at 3,050 kgm. more than 33° lower than those which I have found. It is impossible to explain this by the effect of any initial impurity; a possible explanation is that the design of Tammann's apparatus was such as to allow contamination by the fluid transmitting pressure.

Besides the values of Tammann, there are several other values for comparison at atmospheric pressure. For the melting point we have 50° by Kopp,[33] 49.5° by Bruner,[34] 51° by Bartoli,[35] 52.5° by Stohlmann,[36] and 54.0° by Weger.[37] These wide variations of melting point emphasize the difficulty of getting this substance pure. For the latent heat, there is one value by Bruner,[34] who gives 18.30 kgm. m. against 21.03 above. Bruner's sample was very impure, as shown by its melting point of 49.5°. The change of volume at atmospheric pressure has been measured by Block,[11] working in Tammann's laboratory. But his sample was also impure, as indicated by the low melting point, 51.4°; the impurity may have been the same as that of Tammann's sample. He gives for the change of volume 0.0813 cm.^{3} per gm., against 0.1453 above. This enormous discrepancy can be due only to impurity, and emphasizes the necessity for having pure samples for determining the change of volume. It is to be remembered that the value which I obtained with the first impure sample was somewhat lower than that found for the pure one.

Bismuth.—Especial interest attaches to the melting curve of bismuth because, apart from the fact that it is an element, it is one of the few substances whose melting is of the ice type, that is, the volume of the solid is greater than that of the liquid. The question of greatest interest is whether there is a second modification of the solid denser than the liquid analogous to ice III. We are also interested to know whether the melting curve is concave downward, whether the change of volume increases along the melting curve, and whether the latent heat diminishes, as it does for the ice I curve. So far as I know, water is the only other substance of this type whose melting curve has been hitherto determined. The melting curve of bismuth has been previously measured by Tammann[38] and by Johnston and Adams,[39] but the pressure range of these

33. H. Kopp, Lieb. Ann., *95*, 307–356, 1885.
34. L. Bruner, Ber. D. Chem. Ges., *27*, 2102–2107, 1894.
35. A. Bartoli, Gazz. Chim. Ital., *24* (2), 156–172, 1894.
36. F. Stohlmann, Jour. prak. Chem., (*2*), 40, 341–364, 1889.
37. F. Weger, Lieb. Ann., *221*, 61–107, 1884.
38. G. Tammann, ZS. anorg. Chem., *40*, 54–60, 1905.
39. J. Johnston and L. H. Adams, Amer. Jour. Sci., Vol. 31, 501–517, 1911.

investigators was not high enough to enable them to tell the direction of curvature, and they made no measurements of the change of volume, and so, of course, were not able to calculate the latent heat.

The bismuth was Kahlbaum's purest, used without attempt at further purification. The purity of the specimen was not perfect, because there was some rounding of the corners of the melting curve, but it was only slight.

The previous temperature range of this work has been to only 200°, but the melting point of bismuth at atmospheric pressure is about 270°, so that some modification in the temperature bath became necessary. It was found that the same bath liquid, "Crisco," could still be used for the higher temperatures, provided that a tight cover was placed over the tank to prevent the escape of the stifling smoke into the air of the room. The temperature control was the same as before, by means of a mercury in glass thermostat, which regulated the supply of gas. The temperature regulation by the thermostat was not quite so good at the higher temperatures as it was at the lower ones. The variation of temperature was in some cases as high as 0.7°, or it might be as low as 0.2°. The mean of the extreme values was taken as the temperature of the experiment; this must be very close to the true value at the inside of the heavy steel cylinder. A modification of the method of measuring temperature was also necessary, because the Reichsanstalt calibration of the mercury in glass thermometers used in the previous work reached only to 200°. For this purpose a platinum resistance thermometer was used. This was one that had been constructed by Dr. H. M. Trueblood in this Laboratory for use in his measurements of the Joule-Thomson effect in steam. For this work, I calibrated the thermometer again in ice, boiling water, and boiling naphthalene. For the boiling point of naphthalene and the effect of the barometric pressure upon it, the values of Johnston and Adams[40] were used.

Two sets of measurements were made. The first was with a cylinder which had previously developed a flaw, but which had been patched with apparent success. The flaw redeveloped, however, at about 6,000 kgm. so that the cylinder had to be scrapped. On computing the values for the change of volume from this first run, it appeared that there had always been some minute leak at even the lowest pressures, so that the results had to be discarded. The equilibrium points of this first run up to about 6,000 kgm. were consistently 1° higher than those of the second run. The explanation of this is probably connected with the extreme slowness of the reaction. To meet this difficulty a special method of procedure was

40. L. H. Adams and J. Johnston, Amer. Jour. Sci., Vol. 33, 534–545, 1912.

adopted during the second run. The second run, made with a new cylinder, was over the entire pressure range up to 12,000 kgm. and was successful in every way. It was gratifying to find that the cylinder would stand the maximum pressure at the higher temperature. During the seasoning of the cylinder, the pressure was pushed to 13,000 at 220°.

The reaction, whether melting or freezing, was very slow at the upper end of the curve. Part of the explanation of this is to be found in the small slope of the melting curve and the low latent heat, but this does not seem sufficient to entirely explain the unexpected slowness of the reaction. The appearance was as if the heat conductivity of the cylinder has become very much less at the higher temperatures. Whatever the explanation, a source of error was found here which I have never observed before at the lower temperatures. To explain the possibility of error, let us suppose that pressure has just been decreased so as to carry the liquid into the region of the solid. Freezing takes place with rise of pressure, accompanied with setting free of heat and rise of temperature. If now, before equilibrium has been completely attained, the pressure is artificially raised, we may get the reverse reaction, that is, a fall of pressure, at a pressure that is lower than the true melting pressure at the temperature of the bath, because the temperature of the inside of the cylinder is higher than that of the bath. This gives the appearance of having shut the equilibrium pressure within two limits, at one of which the pressure rises while at the other it falls, whereas the fall of pressure would have taken place only at a higher pressure if temperature had been completely attained. To avoid the error, one must take especial pains to wait for complete equilibrium. But this would require a very long time at the higher temperatures of the range, perhaps three or four hours from one side only. Apart from the tediousness of the operation, the error from slight changes in the bath temperature during this interval would more than counterbalance any other gain in accuracy. Another procedure was adopted therefore. Pressure was first lowered far enough beyond the equilibrium line to ensure the reaction running partly, so that both phases were present in the apparatus. By moving the piston, the pressure was then raised back to nearly the equilibrium value, and then further slight changes made until pressures were found at which the pressure would fall or rise after a change. The advantage is that a very slight amount of reaction can be detected in this way and then the pressure altered in the correct direction, before there is time for much of the heat of melting to be set free. By careful work, the equilibrium point, both from above and below, can be found in less than an hour by this method, and very much more accurately than by waiting for the pressure to automatically restore itself over the entire range.

A very striking change in the reaction velocity was found below 250°. Below this temperature the reaction becomes as rapid as a normal melting reaction for metals in this type of apparatus, and no such special procedure was necessary as above. No marked change in the thermodynamic properties of bismuth takes place at 250°, judging from the melting curve; if the effect is due to a change in the properties of the bismuth, it must be some molecular change too far below the surface to affect the ordinary thermodynamic properties. If the effect is due to the bismuth, it is difficult to understand how other experimenters have been able to get a sharp melting point at atmospheric pressure by observing

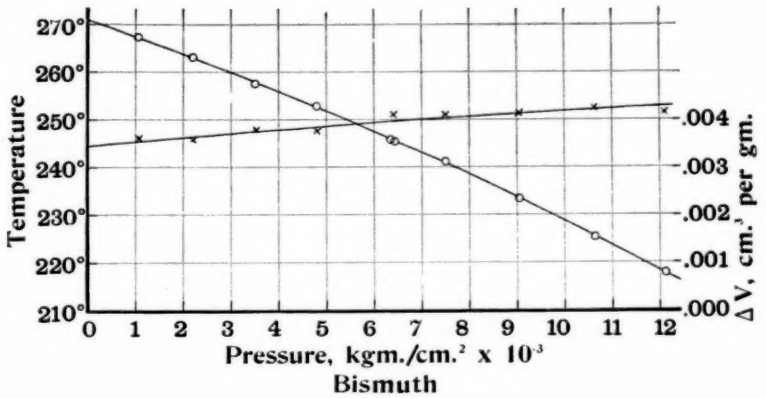

Fig. 18.

Bismuth. The freezing curve and the change of volume curve. The circles show the observed freezing temperatures and the crosses the observed changes of volume.

the arrest point in the cooling curve. It seems very possible that the effect is not one inherent in the bismuth, but may be due to a change in the thermal conductivity of the kerosene or the steel cylinder. The steel was of chrome-vanadium steel; the cylinders in both the preliminary and the final runs were made of this, and the effect was found both times. There may be some molecular change in the steel at this temperature. The manufacturers recommend heating the steel to 270° to draw the temper.

The observed points and the curves for melting and change of volume are shown in Fig. 18, the computed values for the latent heat and the change of internal energy are shown in Fig. 19 and the numerical values are collected in Table VIII. It is to be noticed that everything is exactly the same as it is for ice I. The melting curve is concave downward, the change of volume curve rises with increasing pressure, and the latent heat and the change of energy become less at the higher pressures. The significance of the rising ΔV curve, unless the dilation relations of solid

TABLE IX.

Bismuth.

Pressure.	Temperature.	ΔV Cm.³/Gm.	$\frac{d\tau}{dp}$	Latent Heat, Kgm. M./Gm.	Change of Energy, Kgm. M./Gm.
	°				
1	271.0	0.00345	−0.00342	5.49	5.49
1,000	267.5	354	357	5.36	5.39
2,000	263.8	362	372	5.24	5.31
3,000	260.0	370	387	5.11	5.22
4,000	256.0	378	403	4.98	5.13
5,000	251.9	386	418	4.85	5.04
6,000	247.6	394	434	4.72	4.96
7,000	243.2	401	451	4.59	4.86
8,000	238.6	407	469	4.44	4.76
9,000	233.8	413	487	4.30	4.67
10,000	228.8	419	506	4.16	4.58
11,000	223.6	424	525	4.01	4.48
12,000	218.3	429	545	3.88	4.39

and liquid are very abnormal, is that the solid is more incompressible than the liquid, although it has a larger volume. It was a matter of great surprise that no other modifications were found. It is almost inconceivable that the liquid should remain permanently of smaller volume

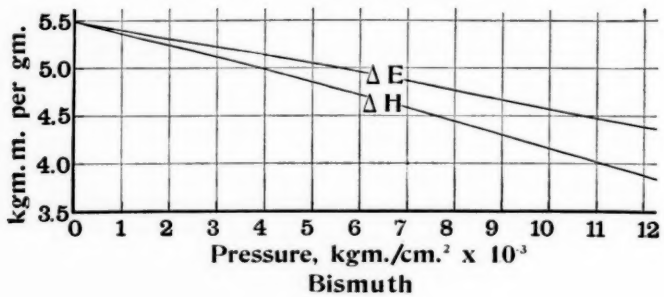

Fig. 19.

Bismuth. The computed values of the latent heat and the change of internal energy when the solid melts to the liquid.

than the solid; if we could apply enough pressure we must force the liquid to crystallize into another modification of smaller volume. We must remember, however, that the internal pressure in a metal is already very high, so that we need not be surprised if a very great additional pressure is needed to make it assume another form. It may be mentioned that these experiments show that the effects observed by Ludwig,[41] which he explained by the production of another modification of bismuth under a pressure of 10,000 kgm., must have their explanation in some other direction.

41. A. Ludwig, Jour. Amer. Chem. Soc., Vol. 31, 1130–1136, 1909.

There are several other values for comparison. The melting curves under pressure have been measured by Tammann[38] to 3,000 kgm. and by Johnston and Adams[39] to 2,000 kgm. Tammann gives the melting point at atmospheric pressure as 269.2° and the change of melting temperature with pressure as − 3.9° for 1,000 kgm. Johnston and Adams find for the melting temperature 271.0°, and for the change of melting temperature with pressure − 3.55° for 1,000 kgm. I find by extrapolation 271.0° for the melting point at atmospheric pressure, and for the average slope of the melting curve over the first 2,000 kgm. − 3.60° for 1,000 kgm., agreeing with Johnston and Adams within their limits of error, which they state as 0°.08. Other values of the melting point at atmospheric pressure are: 270.5° on the mercury, and 266.8° on the air thermometer by Person,[42] 271.0° by Vicentini and Omodei[43] on the air thermometer, and 269.2° from an unknown source quoted by Callendar[44] in a table of fixed points. For the change of volume on freezing at atmospheric pressure there are: 0.003 to 0.005 cm.^{3} per gm. by Nies and Winkelmann,[45] 0.0023 by Roberts and Wrightson[46], 0.003 by Lüdeking,[47] 0.00344 by Vicentini and Omedei,[43] and 0.00336 to 0.00340 by Toepler.[48] In criticism of some of these values it may be said that the bismuth of Nies and Winkelmann was admittedly very impure, the individual observations of Roberts and Wrightson show wide variations, and the bismuth of Lüdeking was known to be impure with a small amount of mercury and its melting point was about 260°. There seems to be only one determination of the latent heat of melting, 12.6 gm. cal. by Person.[42] The value given in the table above is 12.7 cal. The agreement is better than one has a right to expect when one considers the known errors in Person's work, which was performed before modern accurate methods in calorimetry had been introduced.

This completes the list of liquids whose melting curves have been systematically investigated. In addition to these, several others were examined without result for other solid forms, and incidentally some of the melting data were collected. These are now given.

Menthol.—This was from Eimer and Amend, purified by distillation. An attempt to further purify it by crystallization in the thermostat failed; the crystal growth does not take place in the form of large single

42. C. C. Person, Ann. Phys. et Chim., *76*, 432, 1849.

43. G. Vicentini and D. Omodei, Atti Torino, *22*, 28–47 and 712–726, 1886–87; *23*, 38–43, 1887–88.

44. H. L. Callendar, Phil. Mag., Vol. 48, 519–547, 1899.

45. F. Nies and A. Winkelmann, Wied. Ann., *13*, 43–83, 1881.

46. W. C. Roberts and J. Wrightson, Brit. Assoc. Rep., 1880, 544.

47. C. Lüdeking, Wied. Ann., *34*, 21–24, 1888.

48. M. Toepler, Wied. Ann., *53*, 343–378, 1894.

crystals, but confused aggregates of crystals, in appearance like mould, separate out. The melting point was not carefully determined; it was, however, somewhat higher than 42°, because no trace of melting took place at this temperature in 16 hours in the thermostat. The melting point of the pure substance is given as 42.40° by Hulett,[17] and 42.0° by Bruner.[16] The change of volume on freezing at 77 kgm. was found to be 0.0612 cm.^{3}/gm. The latent heat of menthol is given as 18.9 cal. by Bruner.[16] If we combine my value for ΔV with Hulett's value for $d\tau/dp$, (= 0.0245), we obtain for the latent heat 18.5 cal. At room temperature no new modification of the solid was found to 12,000 kgm.; no other temperature was tried. Menthol is known to have an unstable modification, and Hulett has determined its melting curve to 300 kgm. This modification did not appear during the present work.

Anethol.—This was from Eimer and Amend, purified by distillation and by repeated fractional crystallization at room temperature. This was possible because the normal melting point is very close to room temperature. In spite of repeated crystallizations, a substance with sharp freezing was not obtained. The melting point was not carefully determined; it was somewhat over 20°, whereas the melting point of the pure substance is given as 21.3° by Schiff,[22] 21.65° by Landolt,[49] and 22.3° by Block.[18] The change of volume found at 77 kgm. was 0.0793 cm.^{3}/gm. Block gives 0.0794 at atmospheric pressure. Eykmann[20] gives 27.9 cal. for the latent heat. Combining this with a value 0.0800 for the change of volume at atmospheric pressure, gives 0.0194 for $d\tau/dp$. The melting pressure at 100° was found to be in the vicinity of 4,200 kgm. At room temperature there were no new modifications to 12,000 kgm. and none between the melting point and 12,000 at 100°.

Naphthalin.—This was Kahlbaum's purest, redistilled. The melting point was not determined. No new modification was found up to 12,000 kgm. at room temperature or 200°. At 200° the melting pressure is roughly 4,000 kgm. This agrees with the value extrapolated from Tammann's curves. J. Johnston, at the Geophysical Laboratory in Washington, has recently made a careful measurement of the melting curve of this substance (his results are not yet published), so there was no particular object in repeating the measurements here.

Acetophenone.—It was mentioned in the preceding paper[1] that this had not been successfully purified, so that it was not worth while to attempt the determination of the melting curve. The impurity present was sufficient to depress the freezing point from 20.5° to 19.6°. This impurity was not present in sufficient amount, however, to make it seem

49. H. Landolt, ZS. phys. Chem., *4*, 349–371, 1889.

useless to try if there were other solid modifications. No other forms were found, however, to 12,000 kgm. at room temperature or 200°. At 200° the melting pressure is approximately 11,600 kgm., and the change of volume 0.0454 cm.^{3}/gm.

Antimony Tri-iodide.—This substance was investigated because it is usually listed as showing an enantiotropic transition point at 113°. This is on the authority of Cooke,[50] who is quoted in the Tables of the French Society as stating that the transition is enantiotropic. Cooke really claims two new forms, one with a transition point at 113°, and a rarer one with a point at 125°. Lehmann, however, in his "Molekular Physik," although listing this among substances with enantiotropic modifications, considers that we are not yet sure that the transition is not really monotropic. Furthermore, Groth, in his "Chemische Krystallographie," says that the subject requires further investigation. Groth is of the opinion that Cooke's two forms are monotropic.

The substance used was obtained from Eimer and Amend, and it was not further purified. It contained considerable impurity. No transition under pressure could be found, although unusually careful search was made. At 20° there was none up to 12,000 kgm., and at 150° none from 12,000 down to 600 kgm.; at 90° there was none between atmospheric pressure and 5,500 kgm., and at 120° none between 400 and 8,000 kgm. Furthermore, on heating SbI_3 in the air, no change of color was observed below the melting point. An attempt to make dilatometric measurements was not satisfactory, because the machine oil used as the medium began to attack the SbI_3 at about the supposed transition point with some evolution of gas. However, it was established that there was no large change of volume near 113°.

In the course of the search for the second modification, the melting point at 200.8° was found to be approximately 1,160 kgm., and the change of volume 0.0240 cm.^{3}/gm. The melting point at atmospheric pressure is 163°.

Sodium.—No new measurements were made on this substance, but recently published values by Griffiths[51] for the latent heat of melting at atmospheric pressure allow a very great improvement upon the values listed in the previous paper[1] for the values of ΔH and ΔE at low pressures. Reference is made to pp. 137 and 158 of that paper for the method used in computing the initial value of the specific heat. Broadly speaking, the method was one of compromise between the values indicated by extrapolation from the high pressure measurements, and the direct

50. Cooke, Proc. Amer. Acad., Vol. 13, 174, 1877.

51. E. Griffiths, Proc. Roy. Soc., Vol. 89, 561–574, 1914.

determinations of other observers. At the time of writing that paper, there was only one determination known of the latent heat, that by Joannis at 13.53 kgm.m./gm. The value indicated by extrapolation from my own work was 12.0, and the compromise value adopted was 12.9. Griffiths' recent value has been determined with great care, and is 11.74, close to the value indicated by extrapolation. The value 11.8

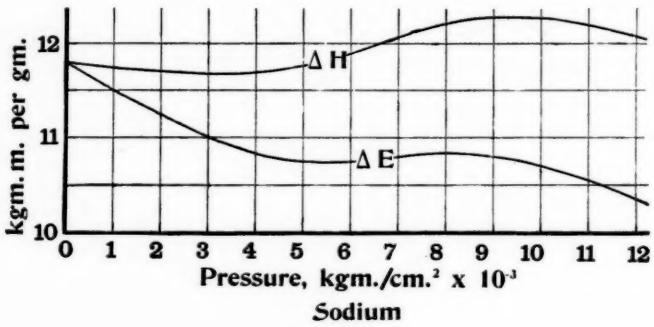

Fig. 20.

Sodium. The latent heat and the change of internal energy when the solid melts to the liquid recomputed from the recent value of Griffiths for the latent heat at atmospheric pressure.

is accepted, therefore, as most probably accurate. This will produce an important change in the values of ΔH and ΔE for the first few thousand kgm., and will remove the initial large and abnormal drop of the curves.

TABLE X.

Sodium [Recomputed Values].

Pressure.	Temperature.	ΔV Cm.³/Gm.	$\frac{d\tau}{dp}$	Latent Heat Kgm. M./Gm.	Change of Energy Kgm. M./Gm.
	°				
1	97.62	0.02787	.00860	11.80	11.80
1,000	105.9	2555	816	11.74	11.50
2,000	113.9	2362	778	11.71	11.25
3,000	121.5	2203	744	11.68	11.01
4,000	128.8	2072	712	11.69	10.84
5,000	135.8	1968	684	11.76	10.75
6,000	142.5	1873	654	11.89	10.75
7,000	148.9	1790	626	12.07	10.80
8,000	155.1	1711	600	12.21	10.84
9,000	161.0	1634	578	12.27	10.80
10,000	166.7	1556	558	11.26	10.70
11,000	172.2	1476	540	12.18	10.54
12,000	177.5	1398	522	12.07	10.35

The recomputed curves are shown in Fig. 20, and in Table X. the recomputed numerical values are listed.

It may also be mentioned that the melting point determined by Griffiths, 96.61°, agrees very closely with the two determinations made above, 97.62° and 97.63°. The agreement is closer than that between any other two observers, and 97.62° may, therefore, be accepted as the most probable value.

A remarkable fact discovered by Griffiths is that the specific heat of the liquid at the melting point is less than that of the solid, a result which holds for almost no other substance. See, however, a later discussion for this matter.

(To be concluded.)

THE MAGNETOSTRICTION AND RESISTANCE OF IRON AND NICKEL.

BY C. W. HEAPS.

THE experiments described in this paper were undertaken with the object of making simultaneous measurements of magnetostriction and resistance in the same specimens of iron and of nickel. The importance of making different experiments on the same specimen is very evident when a comparative study is to be made. The galvanomagnetic properties of a metal are so intimately connected with the other properties such as purity, hardness, crystalline structure, etc., that results of different investigators using different samples cannot be compared with each other with any degree of exactness.

The magnetostriction of iron and nickel has been rather extensively studied by different experimenters, and in a general way all results indicate that a bar of iron has its length increased parallel to the direction of a weak magnetic field and decreased when the field is strong. A bar of nickel suffers a decrease in length for all fields. Different samples of these metals, however, behave differently. Bidwell[1] states that he has obtained in one specimen of iron a contraction for all field strengths and S. R. Williams[2] has observed an initial lengthening in the case of nickel. Whether these diversified results are due to differences in the character of the specimen itself or to differences in the uniformity of the magnetic field applied, one can easily see the necessity of making comparative studies from the same sample under the same conditions.

The importance of considering magnetostriction in connection with resistance is made evident by the failure of theory to explain the effect of magnetization upon resistance without bringing into consideration some term depending on the configuration of the molecules in the metal. A magnetic field may cause the free electrons constituting the current to change their paths and hence the resistance is altered. Also, the magnetic field produces a change in the molecular configuration which further affects the resistance. Magnetostriction must also be associated with a change in molecular arrangement, so that by studying magneto-

[1] Proc. Roy. Soc., Vol. 56, 1894.

[2] PHYS. REV., Vol. 1, p. 257, 1913.

striction one may hope to obtain a clearer insight into the processes of electric conduction.

The apparatus used is shown in Fig. 1. The iron or nickel wires, A and A', each about 8 centimeters long and .022 centimeter in diameter were contained in a glass tube, CC'. By using two wires and a lever, G, the effective length of wire was made 16 cm. They were connected as shown so that by joining the copper rods, K and K', to a suitable Whaetstone bridge the total resistance of the wire could be accurately measured. Changes of resistance produced by the magnetic field were measured by a method of balancing shunts. Since the resistance of the wires was rather small—less than one ohm—it was necessary to correct carefully for the resistance of the leads. The change of resistance of these copper leads in the magnetic field was neglected. The supporting plugs, B and B', were of hard rubber and were firmly cemented into the glass tube. A silk thread extended from the end of A' to the lever, DEF. One leg of the mirror, M, rested on the lever and the other two on a support rigidly attached to the glass tube. The bearings at G and D were of glass on glass. Each bearing was made by melting down the end of a capillary tube till the hole was nearly closed. Into this depression the fine rounded end of the glass axle was fitted. The image of an electric lamp filament was reflected from M upon a scale four or five meters away. Other dimensions were as follows: $FO = 0.2$ cm., $DE = 0.565$ cm., $EF = 3.0$ cm. The magnifying power was calculated to be 32,890. In order to be sure that no disturbing effects were present the wires, A and A', were replaced by silk threads and the apparatus placed in the magnetic field. No deflection resulted when the magnetic field was thrown on or off. Throughout the experiment the weight W was 40 grams and the temperature was that of the room—about 22° C.

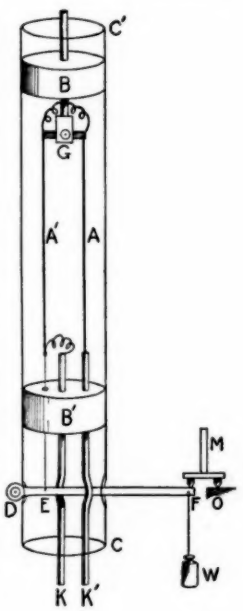

Fig. 1.

The longitudinal magnetic field was furnished by a solenoid 15 cm. long and giving a field of 100 C.G.S. units for a current of one ampere. No attempt was made to correct for the non-uniformity of the field, though this non-uniformity might be quite a factor in the case of such a short solenoid. However, as the resistance and the magnetostriction could be measured without moving the apparatus, any irregularity in the field would probably not affect the value of the data as far as purposes of comparison are concerned.

For producing the transverse field a Weiss electromagnet with pole-pieces 10 cm. in diameter was used. The glass tube of the apparatus was made to have a small diameter so that the pole-pieces could be brought as close together as 1.7 cm. Of course inaccuracy in adjusting the apparatus would introduce a small longitudinal component of magnetization. Jones and Malam[1] have shown that an error of one degree in adjusting the apparatus may affect the results obtained to a slight extent. However, such small errors in the present experiment would not affect comparative study. The magnetic field was measured by the use of a bismuth spiral. The chemical composition of the metals was not definitely determined. Soft Norway iron wire was used in one case. The nickel was of the ordinary kind furnished by Eimer and Amend.

In taking the data it was found inadvisable to make simultaneous observations of resistance change and length change, because the current

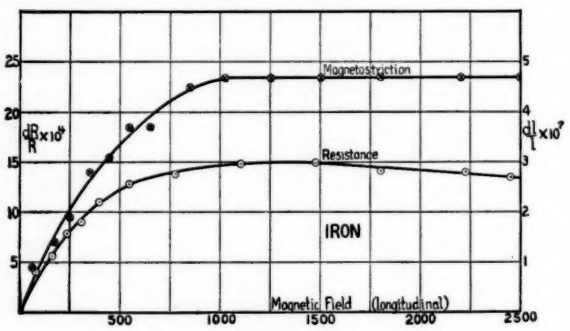

Fig. 2.

through the wire produced disturbing heat effects. Consequently a series of readings for magnetostriction was taken and immediately afterwards a series for resistance. Hysteresis effects were not studied, the observations beginning in every case with a maximum field and ending with the weak field. In the case of nickel the specimen was moved and readjusted between the series of observations, but the accuracy of readjustment was such that any error introduced would be very slight. When iron was used care was taken not to touch the apparatus between observations.

The curves shown are plotted from the data obtained, dl/l being change of length divided by length, and dR/R change of resistance divided by resistance. The external magnetic field measured in gauss is plotted without correction being made for the demagnetizing effect of the metal wires. If the resistance increased, values of dR/R are plotted above

[1] Phil. Mag., Vol. 27, 1914, p. 649.

the axis of abscissæ; while if the length decreased dl/l is plotted above the axis on the same diagram except in Fig. 5, where dl/l reprseents a contraction. The resistance curves are similar in every respect to the ones previously obtained by the writer.[1]

The drop in the resistance curve of Fig. 2 is due to transverse magnetization. It has been shown[2] that with the pure metal and uniform fields there is no initial increase of resistance in a transverse field for either iron or nickel. It is as yet difficult to say whether impurities or a longitudinal component of magnetization is responsible for the initial increase observed in iron in the present experiments.

The magnetostriction curves differ in some respects from the majority

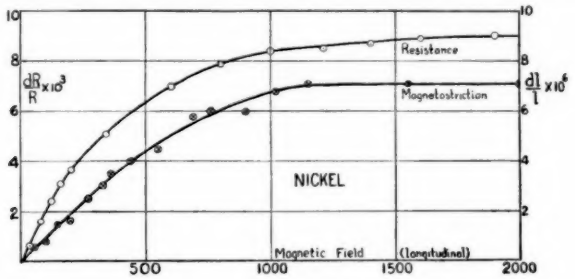

Fig. 3.

of the published results. Iron was found to contract for all values of the longitudinal magnetic field. This contraction is in agreement with one of Bidwell's curves but is at variance with the results of other workers. The transverse field also produced a contraction, though it is possible that in larger fields an elongation might result, as the course of the curve indicates that "saturation" has not been reached at 12,000. In nickel the transverse field produced an elongation and the longitudinal field a contraction.

In Figs. 2 and 3 there is remarkable parallelism between the resistance curves and the magnetostriction curves. An increase of resistance is associated with a decrease of length, and it seems probable that whatever causes operate to change the resistance also operate according to much the same law to change the length of the conductor. According to Drude's theory of metallic conduction the electric current is given by

$$I = \frac{1}{2} N \frac{e^2}{m} X \frac{L}{u},$$

where N is the number of electrons per unit volume, X is the electric force, u the average velocity of the electrons, and L the mean free path.

[1] Phil. Mag., Dec., 1911, p. 900.

[2] Jones and Malam, l. c. R. A. Heising, PHYS. REV., Vol. IV., 4, 1914, p. 315.

This equation is usually assumed to hold true even in the newer theories of metallic conduction, where application of the quantum hypothesis is made. Presumably, by changing the arrangement of the molecules, the longitudinal magnetic field affects L. If L is made smaller the resistance is increased. Let I' be the current when the magnetic field acts. Then

$$I' = \frac{1}{2} N \frac{e^2}{m} X \frac{L'}{u} = \frac{X}{R'},$$

where L' is the new free path and R' the new resistance. Subtracting this equation from the first gives

$$\frac{1}{R} - \frac{1}{R'} = \frac{1}{2} \frac{Ne^2}{mu} (L - L')$$

or

$$\frac{dR}{R} = \frac{dL}{L}.$$

Here dL is the decrease in L while dR is the increase in R. It seems reasonable to suppose that when the intermolecular distances are made smaller the length of the conductor as a whole should decrease proportionally. That is, we might expect

$$\frac{dL}{L} = C \frac{dl}{l},$$

where C is a constant and l is the length of the conductor. Hence,

$$\frac{dR}{R} = C \frac{dl}{l}.$$

In Fig. 6 the values of dR/R are plotted against corresponding values of dl/l. In the case of iron a straight line results as is to be expected from the above theoretical considerations. No values are taken from the resistance curve for fields above 1,200, as transverse magnetization causes a drop above that point. The curve of Fig. 6 for nickel is also a straight line for large fields but for small fields the law of direct proportionality no longer holds. W. A. Jenkins[1] has studied magnetostriction and resistance in different specimens of nickel and he comes to the conclusion that dR/R is proportional to $\surd dl/l$ for fields below 100 C.G.S. units. For larger fields than this the law will not hold. Data taken from the observations of other experimenters do not support Jenkins' conclusion, though, as was pointed out above, data obtained from different samples may give different results. The crystalline structure of a nickel rod may be quite different from that of a drawn wire. However

[1] Phil. Mag., Vol. 27, 1914, p. 731.

it seems possible that in the case of nickel one cannot assume the change of intermolecular distance for small magnetic fields to be proportional to the total change of length as in iron.

In the case of a transverse magnetic field two factors enter to change the resistance—(1) the molecular rearrangement, and (2) the direct

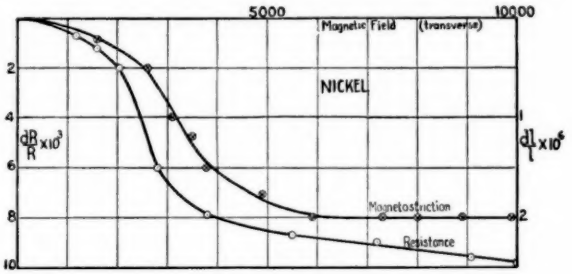

Fig. 4.

deflection of the electrons by the magnetic field.[1] We would therefore expect the magnetostriction and resistance curves of Figs. 4 and 5 to resemble each other only when term (1) is large compared with term (2). This seems to be the case in the nickel specimen studied, though even here the effect of term (2) is evident. When the magnetic field is made

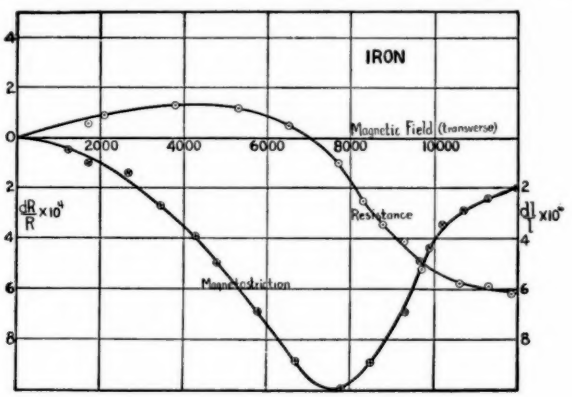

Fig. 5.

as large as 6,000 the molecular rearrangement is complete and the length ceases to increase. The resistance, however, continues to decrease slightly as the field increases, and this decrease must be attributed to the magnetic deflection of the electrons.

[1] For a longitudinal field (2) also produces an effect, but it is smaller than for a transverse field. The writer has calculated the magnitude of (2) to be $\frac{1}{36} H^2 \frac{e^2}{m} T^2$ for a longitudinal field. For a transverse field it is $\frac{1}{4} H^2 \frac{e^2}{m} T^2$. (E. P. Adams, PHYS. REV., May, 1907, p. 428.)

The curves for iron (Fig. 5) show that the molecular rearrangement is not complete for fields as large as 12,000. That is, the length change is still dependent on the magnetic field when it has that value. This would seem rather surprising were it not probable that the intensity of magnetization and not the magnetic field is the factor which determines the form of the curves, and it is much more difficult to magnetize wires transversely than longitudinally. The complex nature of the magnetostriction curve for iron would lead one to expect a complex resistance curve, such as is shown, especially if the two factors mentioned above as determining the resistance change are simultaneously operative. It is perhaps significant that as long as a transverse magnetic field produces an increase in the resistance of iron the contraction of the iron increases. When the resistance change becomes negative the contraction begins to decrease in magnitude.

In all of the curves except those of Fig. 5 the resistance increase is coupled with a length decrease, and vice versa, and for iron the tendency is towards this relation as is pointed out above. Guthe and Austin[1] have found an increase in the length of Heusler alloy placed in a magnetic field. The previous experiments[2] of the writer on this metal have shown that the resistance decreases, and the curve obtained is similar to the

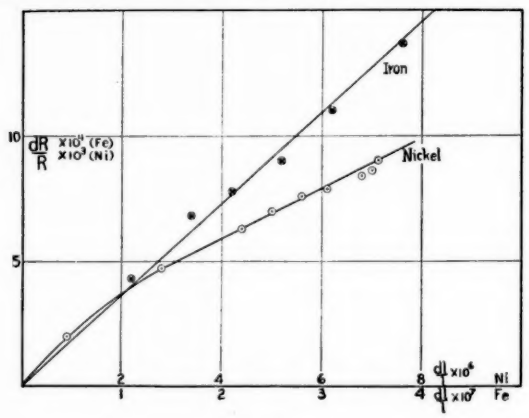

Fig. 6.

magnetostriction curves of Guthe and Austin. Though a law of direct proportionality may not hold good in all cases it is noteworthy that those metals showing large magnetostriction also show a large resistance change. The magnitude of the two effects follows the order: nickel, Heusler alloy, iron. If the analogy holds good for other metals we might expect dl/l in the non-magnetic metals to be of the order 10^{-8} or 10^{-9}.

[1] Bull. Bur. Standards, 2, 297, 1906.

[2] 'Phil. Mag. Dec., 1911, p. 900.

The substitution of experimental data in any of the formulæ derived from our present theories of electric conduction cannot carry one very far on the road towards proving these theories. The mathematical expression for the resistance change in a transverse field is

$$\frac{dR}{R} = \frac{dT}{T} - \frac{1}{4} H^2 \frac{e^2}{m} T^2,^1$$

where T is the free period of the electrons in the metal. Various attempts have been made to explain experimental results using this equation—Jenkins finding it unsatisfactory and Jones and Malam meeting with fair success. It is doubtful whether sufficient data can be obtained to justify numerical substitutions in the above equation since H cannot properly be taken as the external magnetic field or the magnetic induction. It is more proper to consider it as corresponding to the "molecular field" of Weiss's magnetic theory, and the changes produced in this molecular field by an external field must be of a very complex character.

The data obtained in this experiment permit of a comparison being made between the longitudinal and transverse magnetostrictive effects, though as has been pointed out by S. R. Williams, the crystalline structure parallel to the length of a wire is different from that perpendicular to the length, so that comparisons cannot be carried too far. If we neglect this factor we find that iron contracts at right angles to the magnetic field as well as parallel to the field. The resulting decrease of volume per unit volume is of the order 10^{-6}. Nickel expands perpendicularly to the field and contracts in the direction of the field. The calculated maximum decrease in volume of nickel is 3×10^{-6}. These conclusions are in contradiction to the experiments of Nagaoka and Honda who found an increase in volume for both iron and nickel.

S. R. Williams, in a series of recent articles, has sought to attribute magnetostriction to the orientation of molecular magnets having the form of oblate spheroids. For this theory to hold good transverse elongation of a conductor would have to be associated with longitudinal contraction, and vice versa. In nickel this is the case, but in iron the phenomena seem to be of too complex a nature to allow of such a simple explanation. It is probable that some sort of structural modification takes place in which the molecular grouping is changed by the magnetic field, and this changed molecular grouping may be taken in connection with a theory of oblate spheroids to explain most of the phenomena observed.

[1] E. P. Adams, PHYS. REV., May, 1907, p. 428.

SUMMARY.

1. The specimen of iron was found to contract when magnetized either transversely or longitudinally.

2. The specimen of nickel contracts in the direction of a magnetic field and expands perpendicularly to the magnetic field.

3. For a longitudinal field the magnetostriction and resistance curves are found to be very similar—in iron the resistance increase is proportional to the contraction.

4. For a transverse field the magnetostriction and resistance curves of nickel are very similar, showing a close relationship between the two effects. In iron the relationship is also evident, but is more complex than in the case of nickel. A decrease of resistance is associated with a diminution of magnetostriction, and an increase of resistance with an increase of magnetostriction.

5. Except with iron in a transverse field contraction is always coupled with an increase of resistance and expansion with a decrease of resistance.

6. Application of the electron theory to the experimental results is as satisfactory as could be expected, though ignorance of the laws governing intermolecular actions in different metals prevents to a considerable extent the testing out of any theory.

THE RICE INSTITUTE,
HOUSTON, TEXAS.

A MODIFIED VARIABLE CONDENSER FOR USE WITH THE QUADRANT ELECTROMETER.

BY HARRY CLARK.

IN the use of the quadrant electrometer to measure very small currents the best results are obtained by the use of a compensation method, that is, one in which the current to be measured is neutralized by an equal current of opposite sign produced in such a way that its value may be calculated. Thus the electrometer is used only as a detecting instrument and its quadrants remains always at zero potential.

Such a current may easily be produced either by the use of a quartz piezo-éléctrique or by a condenser, one terminal of which is connected to the electrometer while the potential of the other is regulated in any convenient way. The *standard condenser method* consists in varying this potential between known limits while the capacity is kept constant. In the *variable condenser method* the potential remains fixed while the capacity is varied. By any of these methods a known quantity q of electricity is delivered to the electrometer at any desired rate, and the average value of the current is given by q/t where t is the interval of time during which compensation is effected.

Ideally the procedure in making a measurement might be as follows: The unknown steady current is deflected into the insulated quadrants of the electrometer, and at the same instant the chronometer is started and compensation is begun. The spot of light is held at zero by careful manipulation of the compensating apparatus until the whole charge q (depending on the limitations of the particular apparatus used) has been delivered, at which instant the chronometer is stopped.

It is difficult for the operator whose attention is fixed on the spot of light to anticipate this latter instant. He must therefore stop the chronometer without warning. Since it is also difficult to keep the needle exactly on zero, he cannot be sure that the quadrants were at zero potential precisely at that instant.

In practice much better results are obtained with less fatigue to the observer by adopting the following slightly varied procedure: the current to be measured is deflected into the electrometer and the spot of light is allowed to depart from its zero position. As it passes some convenient

point, say the one-centimeter mark, the chronometer is started. Compensation is then begun, and the spot of light is brought back to zero and held there as nearly as may be until the entire compensating charge has been delivered. The spot of light again departs from zero, and as it passes the one-centimeter mark the chronometer is stopped. Slight irregularities in the movements of the needle, due to faulty manipulation, are thus partly damped out, and the instants of starting and stopping the chronometer are sharply defined. If measurements made in this way are to be accurate, both the starting and stopping of the chronometer must be retarded by the same amount, which will be true only in case the capacity of the apparatus has the same value at the end of the experiment as at the beginning. While this requirement is fulfilled by both the quartz piezo-éléctrique and the standard condenser, it is obviously unsatisfied by the ordinary variable condenser.

The method to be described overcomes this difficulty completely. It consists essentially in the use of two variable condensers. One terminal of each condenser is connected to the insulated quadrants of the electrometer, the other terminals being maintained at potentials V and zero respectively. The entire compensation current is produced by varying the capacity of the first condenser. If the second is varied at such a rate that the sum of the two capacities remains constant the sensitivity of the apparatus will not be changed.

As used by the writer these two condensers are combined into a single instrument indicated in Fig. 1. The fixed plates at A serve as a common electrode for both capacities and communicate with the electrometer, D, and the source, G, of the unknown current. The movable piles of semicircular plates, B and C, though rigidly mounted on the same support and constrained to rotate together, are insulated from each other. B is kept at any desired potential by means of a battery F, while C is put to earth.

Some of the details of the apparatus may be seen in Figs. 2, 3, 4, and 5 which are about one fifth actual size. The pile of fixed plates shown at the right in Fig. 5 consists of two pairs separately supported and insulated with amber. By means of the platinum-tipped screw seen at the left in Figs. 2 and 4 it is possible to connect one or both pairs to the electrometer, thereby greatly increasing the range of usefulness of the instrument. The movable piles communicate with the battery and earth respectively through small spiral springs shown in Fig. 3. All metal parts save the central steel shaft which is completely enclosed are made of the same metal, brass, to reduce the Volta effect, and the trouble from accidental charges on insulators is reduced to a minimum by screening.

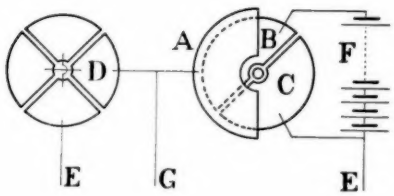

Fig. 1.

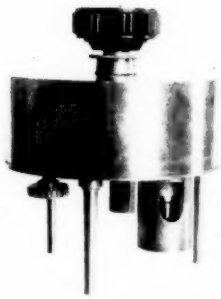

Fig. 2.

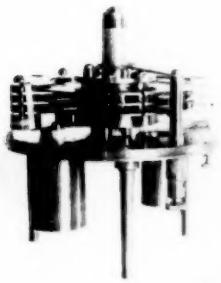

Fig. 3.

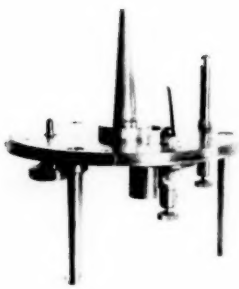

Fig. 4.

Fig. 5.

HARRY CLARK.

The advantages of this modified variable condenser method are obvious. By comparison with the quartz piezo-éléctrique the apparatus is cheaper, less fragile, better insulated and less sensitive to moisture, has any desired range of values, and is much more easily manipulated and less fatiguing to the operator especially in measurements of long duration. The standard condenser method requires a potentiometer operating continuously or nearly so over a wide range of voltage and such instruments usually consume an appreciable current and are difficult to use. The variable condenser uses so little current of course that very small cells may be employed, small cadmium cell for example. The apparatus described in this paper has been used by the writer and has been found to operate consistently with no appreciable error, certainly better than two parts in a thousand.

The writer desires to extend thanks to M. Jacques Danne of Gif, S-et-O, France, in whose laboratory the idea of the modified condenser was partly worked out.

JEFFERSON PHYSICAL LABORATORY,
CAMBRIDGE, MASS.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

WASHINGTON MEETING, APRIL 23 AND 24, 1915.

MINUTES OF THE SEVENTY-SEVENTH MEETING.

A REGULAR meeting of the American Physical Society was held at the National Bureau of Standards, Washington, on Friday and Saturday, April 23 and 24, 1915.

Friday, 2:00 P.M.

Hon. William C. Redfield, Secretary of Commerce, opened the meeting with a cordial address of welcome in which he gave strong expression to his interest in the progress of science, and his belief in the vital interdependence of physics and the commercial interests of the country.

Papers were presented as follows:

On the Distributed Capacity of Single Layer Solenoids. (By title.) J. C. HUBBARD.

The Skin Effect in Bimetallic Wires. JOHN M. MILLER.

Magnetization by Rotation. S. J. BARNETT.

Intercomparisons of the Standard Instruments at Magnetic Observatories, 1905–1914. L. A. BAUER.

Simultaneous Readings in Electrical Measurements, with Demonstration of a New Type of Switch for Facilitating Them. WALTER P. WHITE.

The General Design of Critically Damped Galvanometers. (By title.) FRANK WENNER.

Apparatus for the Simultaneous Measurement of Length, Electrical Resistance, and Magnetic Permeability as Functions of the Temperature. (By title.) ARTHUR W. GRAY.

The Dielectric Constant of a Heterogeneous Dielectric. H. L. CURTIS AND M. JAMES.

The Separately Excited Electrodynamometer as a Sensitive Galvanometer. ERNEST WEIBEL.

The Crushing of a Hollow Conductor by Lightning. (By title.) W. J. HUMPHREYS.

Aneroid Barometers. M. D. HERSEY.

A Method of Measuring Heat Conductivities. R. W. KING.

Viscosity of Ethyl Ether near the Critical Temperature. A. L. CLARK.

An Equation of State for Normal Substances, Tested in the Vapor Dome. HARVEY N. DAVIS.

The Correction of Echoes in the Auditorium at the University of Illinois. (By title.) F. R. WATSON.

The Transpiration of Plants in relation to Temperature and Solar Radiation. LYMAN J. BRIGGS AND H. L. SHANTZ.

A Mercurial Barometer in which the Well Setting is Eliminated. LYMAN J. BRIGGS.

Saturday, 9:30 A.M.

The Reflecting Power of Metals for the Ultra-Violet Region of the Spectrum. EDWARD O. HULBURT.

The Visibility of Radiation in the Red End of the Visible Spectrum. EDWARD P. HYDE AND W. E. FORSYTHE.

The Effective Wave-Length of Transmission of Red Pyrometer Glasses and Other Notes on Optical Pyrometry. EDWARD P. HYDE, F. E. CADY AND W. E. FORSYTHE.

The Use of a Hollow Filament with Perforations in the Determination of the Black-body-Temperature and True-Temperature Relation for Tungsten. A. G. WORTHING.

A Further Extension of the Spectrum in the Extreme Ultra-Violet. THEODORE LYMAN.

The Fluorescence and Absorption Spectra of Uranyl Nitrate. E. L. NICHOLS AND ERNEST MERRITT.

A Precision Artificial Eye. (By title.) HERBERT E. IVES.

A Flicker Photometer Attachment for a Lummer-Brodhun Photometer Head. E. F. KINGSBURY.

Color Grading and Color Specifications by Means of the Rotary Dispersion of Quartz. (By title.) IRWIN G. PRIEST AND CHAUNCEY G. PETERS.

A Proposed Method for the Photometry of Lights of Different Colors. IRWIN G. PRIEST.

On X-Ray Wave-Lengths. WILLIAM DUANE AND F. L. HUNT.

The X-Ray Spectrum of Tungsten at a Constant Potential. DAVID L. WEBSTER.

Factors Governing the Darkening of a Photographic Plate by X-Rays. J. S. SHEARER.

The Wave-Length Sensibility Curve for Isolated Crystals of Selenium between 200 $\mu\mu$ and 450 $\mu\mu$. L. P. SIEG AND F. C. BROWN.

The Variation of Equilibrium Conductivity of Selenium with the Intensity of Illumination. F. C. BROWN.

The Effect of Variation of Temperature on the Coefficient of Recombination of Electrons in a Selenium Crystal. KATHRYN J. DIETERICH.

Saturday, 2:00 P.M.

A Null Method with Photo-Electric Cells. F. K. RICHTMYER.

New Tests of Einstein's Photo-Electric Equation. R. A. MILLIKAN.

Factors Affecting the Relation between Illumination and Photo-electric Current. HERBERT E. IVES, SAUL DUSHMAN, AND E. KARRER.

The Theory of Adsorption. IRVING LANGMUIR.

The Law of Stokes and the Removal of Particles from Fluids. W. W. STRONG.

Ionization Potential of an X-Ray Tube. E. C. DREW. (Introduced by HORACE C. RICHARDS.)

Parson's Magneton Theory of Atomic Structure. DAVID L. WEBSTER.

A Conducting Paint. M. JAMES.

Mechanical Strain and Thermo-electric Power. WALTER P. WHITE.

Recent Results and Conclusions Regarding Specific Heats at Moderate and High Temperatures. (By title.) WALTER P. WHITE.

Geometrical Tripods and Stands. LYMAN J. BRIGGS.

Changes in Electrical Resistance Accompanying Thermal Expansion, ARTHUR W. GRAY.

The Ballistic Use of a Moving Coil Galvanometer in Measuring Discharges Obeying the Exponential Decay Law. A. G. WORTHING.

The Mobilities of Ions in Air. E. M. WELLISCH.

The Effect of a Magnetic Field on the Initial Recombination of the Ions Produced by X-Rays. (By title.) J. E. M. JAUNCEY.

An Accurate Method for the Measurement of the Conductivity of Electrolytes. (By title.) W. A. TAYLOR AND H. L. CURTIS.

The thanks of the Society were extended to the Washington members for the luncheon generously provided on Saturday for all visiting physicists and to the Bureau of Standards for numerous courtesies extended.

On Friday evening a large number of the members in attendance dined together at the Cosmos Club. This pleasant feature was arranged for and carried out by Dr. L. J. Briggs, of the Bureau of Plant Industry.

The attendance at all sessions was good, and there was considerable profitable discussion of papers. On account of the length of the program, a number of local members courteously yielded their time to others and presented their papers by title only.

A. D. COLE,
Secretary.

NOTE ON THE CONSTRUCTION OF A SHORT VACUUM GAUGE.[1]

BY E. KARRER.

THE gauge herein described is in general form and manner of working exactly like the Gaede gauge. Its construction, however, is simpler and very much more durable, due to the entire elimination of rubber tubing.

The Gaede[2] gauge referred to is well known as an improved McLeod gauge. In the Gaede gauge the mercury reservoir is closed air-tight, so that the mercury column need not be of barometer height, but may be very short.

The reservoir of the Gaede gauge is, as in the McLeod gauge, connected to the compressing chamber by means of rubber tubing. In order to keep this connecting rubber tubing sufficiently flexible and air-tight it is enclosed in another rubber tube which is exhausted.

In the gauge shown in the figure below the mercury reservoir (*lm*) is directly connected to the gas chamber by means of glass tubing. (*cd*) is a capillary tube to facilitate reading the height of the mercury in (*ab*) accurately. (*cd*) and (*ef*) are of the same bore to avoid error due to capillarity. The dimensions of the gauge are as follows:

(*ab*) 23.3 cm. long.

(*cd*) capillary, 1.5 mm. bore, 4.5 cm. long.

(*ef*) capillary, 1.5 mm. bore, 11.5 cm. long.

(*ef*) capillary, 1.5 mm. bore, 11.5 cm. long.

(*gh*) 2 cm.; (*hi*) 7.3 cm. long; (*ik*) 13 cm.; (*kl*) 25 cm.; (*ko*) 41 cm.

Bulb (*fg*) 2.8 cm. diameter.

Bulb (*lm*) 3.2 cm.

Manometer (*vw*) 11.5 cm. long.

(*tu*) is guide for (*ko*), made of 1.5 × 2.3 cm. wood strips.

(*ko*) is made of glass tubing, 1.4 cm. diameter with walls 1.2 mm. thick.

All other parts are made of glass tubing 0.9 cm. diameter, with walls 0.8 mm. thick.

(*i*) is a ground-glass joint, so called "normal," made by Leybold's Nachfolger, Germany.

(*rs*) is wood bearing for the movable tube (*ko*), with spring (*pq*) to keep the ground-joint (*i*) together.

The tube (*ko*) forms with (*ik*) a "T," the end of (*ik*) being ground to fit the end of (*ij*), also ground. The end of (*jk*) is closed and fits in a depression in a brass spring (*pq*) which keeps the ground joint (*j*) together.

To make a determination of pressure the reservoir (*ko*) is raised, rotating about the ground joint as axis, until the mercury stands at a fixed height in (*cd*). The mercury in (*ef*) will stand at a height, depending upon the pressure of the gases which are compressed into it.

[1] Abstract of a paper presented at the New York meeting of the Physical Society, October 31, 1914.

[2] Dr. Anderson, of Baltimore, has pointed out to me that the McLeod gauge may be made to indicate negative pressures. Possibly this is the same phenomenon.

Alongside of (*ef*) is a scale giving the pressure of the gas in the system at the time the gas was compressed into the capillary corresponding to any height of the mercury in (*ef*). This scale gives pressures from 1 mm. to 0.0001. This lower limit was conditioned only by the capillary tube (*ef*) and its bulb, which were taken from the Gaede gauge. The bulb has a capacity of 15 c.c. Gaede gauges may be obtained with a lower limit of .00001. Only certain scale divisions are shown in the figure.

The pressures indicated by the scale are obtained from Boyle's law, after the volume of all portions of the capillary along its full length and the volume of the chamber (*gh*) have been determined. An auxiliary gauge (*vw*) indicates pressures from 100 mm. to 1 mm.

The mercury should always be halted while rising in the capillary tubes, otherwise the mercury in capillary (*ef*) may stand at a higher level and as a consequence indicate pressures much too low.[1] Errors resulting from this cause may be considerable at low pressures. Possibly the cleanliness of the glass surface has something to do with this phenomenon of the lagging of the mercury in the capillary. Tapping the capillary slightly causes the mercury to fall back in such cases.

In filling the gauge with mercury care must be taken to free the mercury reservoir from air as completely as possible by heating the tube. There are several methods that may be followed in filling. Possibly some method as described by Kahlbaum[2] in filling the ordinary McLeod gauge might be followed.

The method used to fill the new short gauge described here was the following: On the end of mercury tube (*ko*) was sealed a stopcock to whose further end was sealed a short tube of large bore. After thorough drying of the tube (*ko*) the cock is opened and the mercury poured in. The stopcock is then closed and the air exhausted while the mercury is heated along its whole length. Whatever air collects at the upper end of (*ko*) near the stopcock may later be forced out by lowering the mercury column with stopcock open. When the mercury has been freed from air, the tube (*ko*) is raised slightly and the gauge exhausted until the mercury falls some convenient distance below the stricture that had previously been made in the bore. At this stricture the stopcock is sealed off. The amount of mercury necessary is less than .5 kg.

The tube (*ko*) might be made of thick-walled tubing of smaller bore, necessitating a much smaller amount of mercury.

A simpler method of filling perhaps would be to disconnect the gauge from the pump entirely and fill like the ordinary mercury manometer by heating and tilting. In this case the end of (*ko*) is sealed beforehand and the bulb may be placed at the extreme end. With this manner of construction the gauge may be made much smaller and lighter, so that it may be more directly attached to the space that is evacuated.

By varying the constricted portion of the tube between the gas volume bulb

[1] Described in circulars of makers, Leybold's Nachfolger, Germany.

[2] Ztschr. f. Instrumentedkunde, XV., p. 192 (1895).

and the ground joint the gauge may be made to act as slowly as desired. When this passage is too large the mercury reservoir must be raised cautiously; otherwise the mercury as it reaches the top of the bulb may splash up into the capillary.

The gauge is entirely free from the annoyances caused by the use of rubber tubing. The mercury is not contaminated by abrasion of the rubber tubing and no leaks will ordinarily develop merely with age, as in any rubber parts.

The tube (*ko*) moves between two guides (*tu*), so that no undue strain is put on the ground joint during manipulation. The guides also afford a convenient support for the hand during the raising of the mercury reservoir.

The chief advantages of the gauge as described in this paper, in addition to those that the Gaede construction affords, viz: large range, sensitiveness,

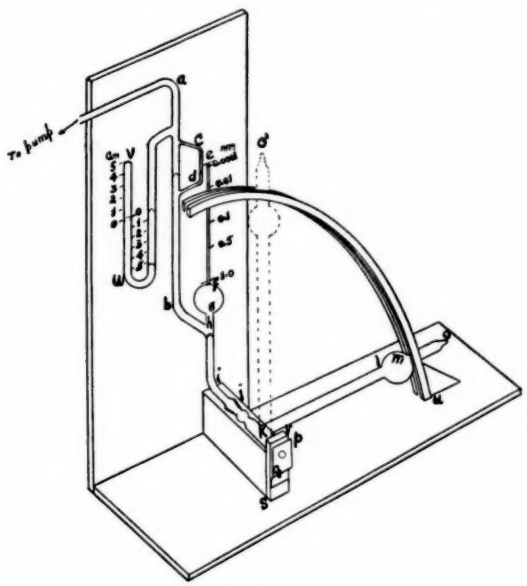

Fig. 1.

direct reading, small size, accuracy and quickness, are simplcitiy, durability and assurance that no portion is liable to disintegrate under ordinary laboratory conditions as rubber parts do.

After the gauge had been constructed and this description written my attention was called to an improved gauge recently described by Reiff.[1]

The gauge described by Reiff is ingeniously designed to eliminate all rubber tubing. However, it is not so simple as the gauge herein described. The article referred to contains an excellent sketch of the development of the McLeod gauge.

Reference is also made to a gauge designed by Rheden,[2] probably very similar

[1] Zeitschr. Instkde., April, 1914, pp. 96–106.

[2] U. Rheden, D. R. G. M., 404499.

to the form of gauge described here. The German patent files in which this is described were not accessible however.

I wish to express my appreciation of the keen interest taken by Dr. H. E. Ives in this work.

Gauges of the design described above are constructed by Ruckstahl and Luchs, Wilkinsburg, Pa.

PHYSICAL LABORATORY,
THE UNITED GAS IMPROVEMENT COMPANY,
PHILADELPHIA, PA.

ELECTRIC FURNACE EVIDENCE ON THE RELATION OF SPECTRUM LINES HAVING CONSTANT DIFFERENCES IN WAVE-NUMBER.[1]

BY ARTHUR S. KING.

PAIRS of lines occur in many spectra for which the differences between the reciprocals of the wave-lengths is very nearly the same for a number of different pairs. These regularities suggest some sort of series relations among the lines, and a comparison of the behavior of the members of such pairs under different physical conditions is of interest in this regard.

Paulson has recently picked out a large number of these pairs of lines, and many of them in the spectra of iron, titanium, and vanadium have been classified by the writer according to their behavior in the electric furnace at different temperatures. In the majority of cases, the members of a pair are in the same furnace class, but the number of exceptions is large enough to be significant. A number of pairs occur for which the component lines are separated by more than one class in the furnace classification. This is greater than the uncertainty involved in the assignment to classes and renders it improbable that both lines in such pairs can be emitted by the same vibrating center. The evidence thus supports the view that these pairs are by-products of series relations, rather than that the lines of the pairs are members of the same undiscovered series.

MOUNT WILSON SOLAR OBSERVATORY,
December 10, 1914.

THE BALLISTIC USE OF A MOVING-COIL GALVANOMETER IN MEASURING DISCHARGES OBEYING THE EXPONENTIAL DECAY LAW.[1]

BY A. G. WORTHING.

FOR the purposes of the present paper, a discharge obeying the exponential decay law has been defined as that discharge which occurs when there is an intrinsic E.M.F. of the exponential decay type in the circuit. Close approximations to such discharges are quite common. Due to the distorting effect of the counter E.M.F. resulting from the generator action of a moving

[1] Abstract of a paper presented at the Philadelphia meeting of the Physical Society, December 29–31, 1914.

coil or a moving needle, the simpler type in which the current obeys a similar law will be rarely met with in practice.

Neglecting the self-induction of the galvanometer circuit—the error in practical cases is usually negligible—the equation giving the ratio of the deflection for an impulsive discharge to the deflection for a prolonged discharge of the same quantity according to the exponential decay law in a so-called radial field, is

$$\phi = \frac{T'}{T} \frac{e^{-2\lambda' \frac{\tau'}{T'}} \sin 2\pi \frac{\tau'}{T'}}{e^{-2\lambda \frac{\tau}{T}} \sin 2\pi \frac{\tau}{T}},$$

where ϕ is the ratio sought, λ, T and τ the logarithmic decrement, the period and the time required for the coil starting at rest to reach its maximum deflection for the case of the prolonged discharge, and λ', T' and τ' the corresponding terms for the case of the impulsive discharge. Theoretical expressions for τ and τ' in terms of the galvanometer constants and of the time-constant of the discharge enable one to obtain the factor ϕ' from easily obtainable data.

For a particular experimental case where $T = T' = 7.35$ sec., where $\lambda = \lambda' = 0.692$ and where the time-constant of the discharge was 1.06 sec., ϕ was found to be 1.296.

By varying the moment of inertia of the galvanometer coil and the resistance in its circuit, several periods varying from 4.3 sec. to 21.5 sec. were obtained in this test. With one exception the computed values for ϕ were found to agree exceedingly well with the observed values.

In case a certain discharge is known to obey the exponential decay law, its time-constant may be determined from observation of the throws obtained with the characteristics of the galvanometer varied as indicated above. That time-constant which leads to a set of values for ϕ which are consistent with the observed throws is the one sought.

This method of obtaining a time-constant has been used with considerable advantage in accuracy in a modification of a method of measuring thermal capacities at incandescent temperatures, given by Corbino, an application of whose method, in attempting to verify certain results reported in November, 1914, led in fact to the present paper.

NELA RESEARCH LABORATORY,
NATIONAL LAMP WORKS OF GENERAL ELECTRIC CO.,
NELA PARK, CLEVELAND, OHIO.

THE MOBILITIES OF IONS IN AIR.[1]

BY E. M. WELLISCH.

THE mobilities of the positive and negative ions formed in thoroughly dried air by the alpha rays of polonium were determined over a wide range of pressures. In the case of the negative ion the results were normal from a

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 23–24, 1915.

pressure of 1 atmosphere down to about 8 cm.; below 8 cm. the negative carriers were found to consist of two kinds, electrons and ions, the former increasing in number relatively to the latter with diminishing pressure. No evidence was found of an intermediate or transition stage, the separation between the faster and the more slowly moving carriers remaining throughout well defined. The mobility of the negative ion was found to vary inversely as the pressure down to the lowest pressure employed ($\frac{1}{7}$ mm.); this indicates that the negative ion remains unaltered in nature over this wide range of pressures.

The positive ion was found to remain unchanged from 1 atmosphere down to $\frac{1}{20}$ mm. which was the lowest pressure tried.

SLOANE LABORATORY,
YALE UNIVERSITY,
April 12, 1915.

PARSON'S MAGNETON THEORY OF ATOMIC STRUCTURE.[1]

BY DAVID L. WEBSTER.

IN a previous paper[2] the author has shown that by means of Parson's concept of the magneton one may eliminate certain serious conflicts of Planck's theory of heat radiation with the phenomena of refraction and related optical effects, and still keep the essential features of Planck's argument. The present paper gives an account of the fundamental concepts of this magneton theory from the chemical point of view from which Parson originally deduced them, but which has not yet been published in full.

According to Parson, the electron, or magneton as he calls it, is not a sphere, but a very thin ring, about 10^{-9} cm. in radius, around which the negative charge circulates at a very high speed, thus combining with its electrostatic properties the magnetic ones of a ring of wire carrying a current.

As Parson has shown, the magnetons in an atom will arrange themselves as far as possible in compact groups of eight. This grouping will explain the periodic table of the elements and the formation of all salts and other compounds whose bonds are electrostatic. The non-electrostatic bonds of organic compounds are explained as a result of magnetic attractions not strong enough to draw a magneton over from one atom into the other. Thus the theory covers a much wider range of chemical phenomena than previous ones, and even includes stability relations and the properties of the elements of the long periods. An added interest is given by the ability of this model to treat also such a widely different class of phenomena as those of radiation, referred to above, and those of optical rotation, for which the author has more recently found it an improvement over previous theories.

JEFFERSON LABORATORY,
HARVARD UNIVERSITY.

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 23–24, 1915.

[2] Proc. Amer. Acad., Jan., 1915.

IONIZATION POTENTIAL OF AN X-RAY TUBE.[1]

BY E. C. DREW.

IN many recent publications the statement is made that the ionization potential of an X-ray tube is very much greater than the running potential, or in other words, it takes a much higher voltage to break down the resistance of the tube than it does to maintain the flow of current, once it is started.

An experimental invsetigation of the point has been made by the author with several standard type tubes. The current through the tube and the fall of potential across the tube are recorded by a loop oscillograph. The measurement of potential by an indirect method eliminates the objection to a direct one, viz: same current through the loop as through the tube. Each loop system is calibrated to read drop or current as required and the instantaneous values of the wave form are scaled off. From the values thus obtained, plots are made which indicate that the ionizing potential is not of the same order generally supposed. The law of current in the tube is not that of Ohm. The energy of ionization and the percentage that this bears to the total energy supplied is not the same in different types of tubes.

RANDALL-MORGAN LABORATORY OF PHYSICS,
UNIVERSITY OF PENNSYLVANIA.

NEW TESTS OF EINSTEIN'S PHOTO-ELECTRIC EQUATION.[1]

BY R. A. MILLIKAN.

THIS paper contains the report of work on lithium of the same sort as that reported a year ago on sodium.[2] The apparatus is however new throughout. Planck's "h" appears as definitely in this work on lithium as it did in that on sodium. There is a very perfect linear relationship between PD and ν and the slope of the line gives

$$h = 6.585 \times 10^{-27},$$

which is within four tenths of one per cent. of the value found with sodium.

The long wave-length limit is found to agree accurately with the intercept on the ν axis of the $PD\nu$ curve.

The observed contact E.M.F. is not found to agree closely with the theoretical value $h(\nu_0 - \nu_0')$ but this may be accounted for by surface in homogeneities.

Einstein's equation is shown to lead to the conclusion that contact E.M.F. is independent of temperature, a result in agreement with recent experiments.

Ramsauer's conclusions are not wholly confirmed by these experiments. The causes for the discrepancies are pointed out.

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 23–24, 1915.

[2] R. A. Millikan, PHYS. REV., Vol. IV., p. 74, 1914.

THE X-RAY SPECTRUM OF TUNGSTEN AT A CONSTANT POTENTIAL.[1]

BY DAVID L. WEBSTER.

IN the spectrum of a Coolidge tube at a constant potential, determined by Duane, Hunt and the author (see preceding paper) the distribution near λ_0 is especially significant. For if the rays were irregular disturbances, they would excite a reflection at any angle, the wave-length of the reflected rays being determined simply by the relative retardations of the waves from the different layers of atoms in the crystal, and the intensity by the extent of the fluctuations in the resulting disturbance; or, as in Schuster's analysis of white light, the intensity may be found from a Fourier series for the incident disturbance. Either way, there would be some intensity at any part of the spectrum.

The fact is, that the intensity is zero for all wave-lengths below the one whose quantum energy is the energy of the cathode particle, and that it suddenly begins to increase on passing that point. Therefore it seems that even in such a spectrum as this, where we are not concerned with any characteristic radiations, the X-ray vibrations are not irregular, but are sent out as trains of periodic waves of all frequencies below the critical one. This, like the evidence from absorption, shows the presence in the tungsten of oscillators of all frequencies. No oscillator can be started in vibration by a cathode electron that does not give it a whole quantum; nor can it take less than that from an electron and hold it until another electron arrives with more, although the production of secondary cathode rays by X-rays indicates that it can absorb continuously from them and store the energy until the quantum is acquired.

JEFFERSON LABORATORY,
HARVARD UNIVERSITY.

THE CORRECTION OF ECHOES IN THE AUDITORIUM AT THE UNIVERSITY OF ILLINOIS.[1]

BY F. R. WATSON.

AN investigation of the acoustical defects of the auditorium at the University of Illinois which has been in progress for a number of years was recently brought to a conclusion when materials were installed to correct the faults. A reverberation and echoes were found to exist. Experiments and calculations by Sabine's method gave means of determining the amount of sound-absorbing material necessary to correct the reverberation. Walls producing echoes were located by means of an arc-light backed by a parabolic reflector.[2] The arc gave forth a hissing sound that traveled with the light so that an observer could see where the sound struck. Small mirrors placed on the walls assisted in tracing the reflected sound.

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 23–24, 1915.

[2] "Echoes in an Auditorium," PHYS. REV., Vol. 32, p. 231, 1911.

Experiments were then carried on in accordance with the analysis. Sounding boards of different sizes and shapes proved to be of small value.[1] Stretched wires[2] and ventilation currents[3] are apparently not effective as means of correcting acoustics. Canvases were hung in various positions in the auditorium to determine the effect of screening certain walls from the action of sound. Absorbing materials were also placed at critical places suggested by the analysis. The final provisional cure was brought about when four large canvases were hung in the dome.

From the acoustical standpoint the auditorium was then in fairly satisfactory shape. The canvas curtains, however, were unsightly and did not harmonize with the architectural features of the room. Steps were taken to find an arrangement that would satisfy both the acoustical and architectural requirements. Complications appeared from the fact that the amount of material necessary to cure the reverberation was insufficient to cover all the walls producing echoes; also, it was decided at this time to install a pipe organ, to change the lighting system and to redecorate the interior walls. Before deciding on the final cure, a preliminary experiment was tried whereby a large curved wall was covered with vertical strips of hairfelt 30 inches wide placed 30 inches apart with bare wall spaces between them. This arrangement had several advantages. It maintained the curvature of the wall and used only half the material necessary to cover the whole surface. Theoretically the incident sound would be broken up because the portions of the waves striking the felt strips would be strongly absorbed and changed in phase. The results obtained were encouraging so other walls were padded in a similar way except that the felt strips were installed one foot out from the wall.

The outcome has been generally satisfactory. The remodeled auditorium has been found to have acceptable acoustics for speaking, pipe organ music, orchestra and band concerts. Weak echoes due to unpadded walls have been reported in several instances but these do not appear to prevent the words of the speaker being understood. The author attributes the successful solution of the investigation in large part to the coöperation and suggestions of Professor James M. White, supervising architect of the university.

Detailed accounts of the investigation with numerous drawings and photographs may be obtained in Bulletin No. 73 on "Acoustics of Auditoriums," published by the Engineering Experiment Station of the University of Illinois, and in a later bulletin on "The Correction of Echoes" which will appear soon. These bulletins will be supplied on application to the author or to the director of the engineering experiment station, University of Illinois, Urbana, Illinois.

LABORATORY OF PHYSICS,
UNIVERSITY OF ILLINOIS.

[1] "The Use of Sounding Boards in an Auditorium," PHYS. REV., Vol. 1 (2), p. 241, 1913. Also a more complete article in The Brickbuilder, June, 1913.

[2] "Inefficiency of Wires as a Means of Curing Defective Acoustics of Auditoriums," Science, Vol. 35, p. 833, 1912.

[3] "Air Currents and the Acoustics of Auditoriums," Eng. Record, Vol. 67, p. 265, 1913.

ON THE DISTRIBUTED CAPACITY OF SINGLE LAYER SOLENOIDS.[1]

BY J. C. HUBBARD.

THE periods of oscillation of circuits consisting of a single layer solenoid and an air condenser have been precisely measured by a method devised for the purpose by the author.[2] One of the objects of the measurements has been to determine the effective, or so-called distributed, capacity of solenoids, special attention being paid to the independent variation of all the factors upon which that quantity might depend. These are the diameter and axial length of the solenoid, the number of turns, the diameter of wire, and the dielectric effect of the insulation and of the core. The period of oscillation is given by

$$T = 2\pi\sqrt{L(K + K_0)},$$

where K is the capacity of the air condenser and K_0 is the remaining capacity of the system, *i. e.*, the capacity of leads and connections and the distributed capacity of the coil. Six values of K, ranging from 200 cm. to 1,500 cm. were used with each solenoid. The periods were measured to one part in two thousand and were of the order of 10^{-5} sec. With all the solenoids used the relation between T^2 and K is found to be linear within the errors of measurement, and accordingly the variation of L with the period is negligible. Hence, for a given solenoid, we may write

$$T^2 = Ka + b,$$

where $a = 4\pi^2 L$, and $b = 4\pi^2 LK_0$, from which, $K_0 = b/a$.

Since $K_0 = K_1 + K_2$, where K_1 is the capacity of the leads and K_2 is the distributed capacity of the coil, we have two independent means of finding K_2, once K_0 is determined for each solenoid. The first is by measuring the capacity of leads and connections, K_1, directly.[3] Whence $K_2 = K_0 - K_1$. The second is to make use of the fact that for geometrically similar electriacl system the electrical constants are in the ratio of the linear dimensions. Thus, if we take two coils, all the dimensions of one being n-fold greater than those of the other, we have, for one

$$K_0 = K_1 + K_2,$$

and for the other,

$$K_0' = K_1 + nK_2.$$

Whence,

$$K_0' - K_0 = (n - 1)K_2,$$

from which K_2 may be found. The results of the two methods are in close agreement. The values of K_2 for the coils used range from 5 to 30 cm. of

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 23–24, 1915.

[2] PHYS. REV., N. S., I., p. 247, March, 1913.

[3] Loc. cit., p. 245.

capacity. The distributed capacity of a single layer solenoid measured in electrostatic units is found to be a number of the same order of magnitude as the radius of the coil, measured in cm., but shows relatively very slight variation with the axial length, number of turns, and diameter of wire. A detailed report of the investigation will shortly be published.

CLARK COLLEGE,
WORCESTER, MASS.

AN EQUATION OF STATE FOR NORMAL SUBSTANCES, TESTED IN THE VAPOR DOME.[1]

BY HARVEY N. DAVIS.

THE equation discussed is

$$\left(p + \frac{a\phi(\theta)}{v^m}\right)(v - b) = RT,$$

the reduced form of which is

$$\left(\pi + \frac{\phi(\theta)}{\omega_0\omega^m}\right)(\omega - \omega_0) = \Delta_c\theta,$$

where

$$\omega_0 = \frac{m - 1}{m + 1}$$

and

$$\Delta_c = \frac{4m}{m^2 - 1}$$

are respectively the limiting reduced orthobaric volume and the ratio of the critical density to the density of a perfect gas, at the critical pressure and temperature. Van der Waals' equation, Dieterici's first equation of 1898, and Dalton's equation of 1914 are special cases of this type. The equation is tested for argon (Crommelin) and for eleven of Young's "thirty substances" selected to cover a wide range of behavior.

If any equation of this type is to be satisfactory, the observed ω_0's and Δ_c's must satisfy a certain relation obtained by eliminating m above. The twelve substances mentioned above, and some fifteen others are shown to satisfy this relation at least approximately, and probably within the limit of error of the observed ω_0's. It is therefore possible to select an m for each substance which will give substantially correct values for both ω_0 and Δ_c.

A partly new mathematical process is next discussed by which the reduced equation can be solved for saturation pressures, temperatures, and volumes, when the form of the function $\varphi(\theta)$ is preassigned. Conversely, one can determine from the experimental data a function $\varphi(\theta)$ that will give exact

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 23–24, 1915.

agreement for any one of the curves, π *vs.* θ, $\omega_{vap.}$*vs.* θ (or preferably $\pi\omega_{vap.}/\Delta_c\theta$ *vs.* θ), and $\omega_{liq.}$*vs.* θ (or preferably $\omega_{liq.}/\omega_{vap.}$*vs.* θ, the latter forms being advantageous in that they do not depend on the observed critical volume). In what follows, the $\varphi(\theta)$ determined from vapor pressures will be used. It appears that it also gives excellent agreement on vapor volumes except in the neighborhood of the critical point. Even there the disagreement is small, and important only from the point of view of the kinetic theory. This $\varphi(\theta)$ will not, however, give as good predictions of *reduced* liquid volumes as will Dalton's equation (with $m = 2$ for all substances), even though Dalton's equation yields an ω_0 and a Δ_c which are greatly in error.

The function $\varphi(\theta)$ is not the same for different substances, but can be put in the form

$$\phi(\theta) = 1 + k\,\Theta(\theta),$$

where the function $\Theta(\theta)$ is the same for all substances, and k is a constant appropriate to each substance. Furthermore, the k's of the twelve substances examined, when plotted against their m's, fall on a smooth curve within the probable limit of error of the critical volumes on which the m's depend. This smooth curve can also be made to pass through the point $k = 0$, $m = 2$, thus making van der Waals' theoretically derived equation one of the singly infinite family of equations that covers the range of real substances.

The fact that the k's form a single-valued function of the m's, means that one can predict with some accuracy the whole course of the reduced vapor pressure curve of a little investigated substance when only its critical virial coefficient is known. If one other point on the reduced vapor pressure curve, say the boiling point, had been available as a check on k, the accuracy of this prediction would have been of the order of a quarter of one per cent. in all but two of the twelve cases examined, and better than one per cent. in those two.

Conversely, it seems probable that the Δ_c of a substance can be predicted to better than one per cent. from its reduced vapor pressure curve. This possibility has not yet been carefully investigated, but it gives promise of developing into a method of determining critical volumes that will be somewhat more accurate and much more convenient than the law of the straight diameter.

A rather sensitive test of an equation of state is afforded by the accuracy with which it can predict latent heats. In this respect van der Waals' equation is very bad, Dieterici's somewhat better, and Dalton's better still. As regards numerical values, the new equation is even better than Dalton's over the observable range of the one substance examined by him, although the shape of the new latent heat *vs.* temperature curve is not quite as satisfactory as his.

Finally, it may be mentioned that this paper puts in an easily tested form an hypothesis already familiar to workers in this field, namely that the law of corresponding states, which is obviously untrue in its original form, is true if one gives it a single degree of freedom by introducing one disposable constant. In this paper the additional constant is the exponent m in the reduced equation of state, and it is found that, at least for ω_0's, Δ_c's, vapor pressures, and values

of the ratio $\omega_{liq.}/\omega_{vap.}$, a one-dimensional law of corresponding states is in substantial agreement with the facts. Indeed the validity of such a law is, apparently, even greater than the validity of the particular form of equation of state that has been discussed.

THE JEFFERSON PHYSICAL LABORATORY,
CAMBRIDGE, MASS.

AN ACCURATE METHOD FOR THE MEASUREMENT OF THE CONDUCTIVITY OF ELECTROLYTES.[1]

BY W. A. TAYLOR AND H. L. CURTIS.

THE purpose of the work, which is now being carried on under a grant from the Carnegie Institution of Washington, to Dr. S. F. Acree, is to develop an accurate method for the measurement of the conductivity of electrolytes in both concentrated and dilute solutions. The work on the problem has been done at the National Bureau of Standards, of Washington, D. C., in order to have the benefit of their excellent apparatus in working out the details of the method. The investigation was begun by Dr. H. C. Robertson, working with Dr. S. F. Acree, at Johns Hopkins University, several years ago, but little definite data were obtained. At Dr. Acree's suggestion we took up three phases of the problem: first, the obtaining of a source of alternating current which is practically free from harmonics and whose frequency can be varied through wide limits; second, the construction of a suitable bridge; and third, the designing of satisfactory cells, and the study of the effect of changes in voltage and frequency on the resistance of electrolytes.

Several commercial generators giving frequencies of 500 cycles or above were tried, but in no case was the wave form sufficiently free from harmonics. A special high frequency generator made by the General Electric Company, giving frequencies from 600 to 3,000 cycles, was much better but did not entirely suit our needs. A Vreeland oscillator was finally adopted because it gives not only a pure sine wave but also an exceedingly steady frequency, which can be changed at will by means of suitable condensers. The oscillator now in use, for which we are indebted to the Leeds and Northrup Co., has a range of frequency of from 150 to 3,000 cycles. It gives a maximum voltage of 54 volts. This voltage is cut down by means of a transformer to voltages suitable for conductivity measurements.

An electrolytic cell behaves toward an alternating current as though it were made up of a capacity in series with a resistance. Hence when used in an alternating current bridge, it is necessary to compensate for this capacity either with inductance or capacity. The apparent capacity of an electrolytic cell is very large, being about 25 microfarads per square centimeter for bright platinum electrodes, and several times as large for platinized electrodes. Hence

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 23–24, 1915.

it is not feasible to compensate by adding capacity in series with an adjacent arm of the bridge. The compensation can be accomplished, however, by using a condenser in parallel with an adjacent arm, but for accurate work this condenser must have negligible losses. This is true only of air condensers and the range of capacity available is small. Hence the most satisfactory method is to use a variable inductance in series with the cell.

To eliminate as many corrections as possible, a substitution method is employed as shown in Fig. 1. R_1 and R_2 are ratio coils of 100 ohms each, S is the resistance in the bridge, R a substitution resistance, C the cell, T the telephone and L a variable inductance. The resistance box R is set on zero, and with the cell in circuit, S and L are varied until there is no sound in the telephone. Then the cell is short circuited and the bridge again balanced by varying L and R. The reading of R is then the resistance of the cell. By working in this way we have found that, under favorable temperature conditions, measurements upon a cell will repeat to one or two parts in a hundred thousand.

The bath used to keep the cells at constant temperature is made of copper and filled with water and it was found that this caused a great source of error from capacity effects, as the value of the resistance in the bridge needed to balance the cell varied considerably, sometimes as much as 0.1 ohm, depending on whether the heating lamps of the bath were on or off. This source of error was eliminated by grounding the bath and also the bridge as in Fig. 1, when there was no difference in the two readings. It was found necessary to move the Vreeland and the transformer for cutting down the voltage to another room as their fields affected the bridge setting. Thus all high potentials should be kept as far as possible from the bridge.

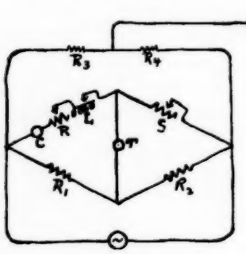

Fig. 1.

We first took up the problem of determining whether there is a change in resistance of a solution of an electrolyte with change in voltage. From the data obtained by the use of many different cells it was found that there is no measurable change in resistance with change in voltage, provided the cells, solutions, and the bottles used to hold the solutions are kept scrupulously clean. The slightest trace of grease or dirt, however, causes a change in resistance with change in voltage. This seems to be a good test for perfect conditions for measurements. The range of voltage was from 1/4 to 4 volts. Above this with the resistances used, the heating effect of the current prevented accurate measurements.

The next part of the work was to determine whether there is a change in apparent resistance with change in frequency. Cells with bright platinum electrodes, varying in size from one half to two inches in diameter were first studied. It was found, as is shown in the table below, that there is a change in resistance with change in frequency, and that this difference depends on the size of the electrodes, the largest electrodes giving the smallest change in

resistance. Thus the two inch sand-blasted electrodes give a smaller change than any others.

The values for the inductance necessary to obtain a balance with the cell are also interesting. From an inspection of the following data it will be seen that as the difference in the resistance between 500 and 1,000 cycles increases the inductance also increases. The data shows one exception to this. It is also seen that the larger the electrode surface the smaller the inductance necessary for a balance.

Size of Electrodes.

	R 1,000 ~.	Ind. 1,000 ~.	Diff. in R at 500 and 1,000 Cycles in Per Cent.
½ inch bright	277.703	2,229	0.744
1 inch bright	310.202	425	0.110
2 inch bright	421.200	134	0.068
2 inch sand blasted	282.092	115	0.025
½ inch platinized	329.769	25	0.000
1 inch platinized	290.269	0	0.000

Decrease in Resistance of Solution.

1 inch bright	310.202	425	0.110
1 inch bright	195.302	350	0.140
1 inch bright	82.834	445	0.477
1 inch bright	55.555	465	0.635
1 inch bright	41.042	550	1.024

These data also show that this change in resistance with change in frequency becomes smaller as the resistance of the solution is increased. This is no doubt due to the fact that we have an electrode effect which becomes a smaller factor as the resistance is increased.

We then took up the study of platinized electrodes. With a cell with one inch platinized electrodes no difference could be detected in the resistance measurements at 500 and 1,000 cycles. With one half inch platinized electrodes, however, we found in concentrated solutions, a small change in resistance with change in frequency, from 500 to 1,000 cycles, although this change was smaller than that for any of the cells with bright electrodes. It amounted to 14 parts in 100,000 for $N/5$ NaCl, but disappeared entirely with $N/20$ NaCl. In the platinized electrodes the surface is very much increased so that the change in resistance with change in frequency seems to depend directly on the size of the electrodes.

In order to try to eliminate this effect of change in resistance with change in frequency with bright electrodes, and thus get the true resistance of the solution in the cell, the following scheme was tried. Measurements were made at three different frequencies, 600, 1,000 and 2,000 cycles, with two cells, both of which had electrodes one inch in diameter, one set of which were bright and the other set platinized. Approximately $N/10$ and $N/20$ NaCl were used in each cell. We then plotted the results as a curve, using the resistance as ordinate and the reciprocal of the frequency as abscissa. By extending

the curves to cut the X axis, we should get the resistances of the solutions at infinite frequency. Using the values of the resistances at infinite frequency we

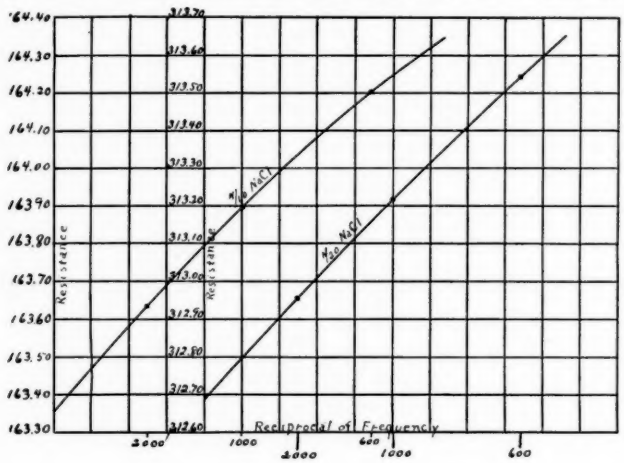

Fig. 2.

found the ratios of the resistances of $N/10$ and $N/20$ NaCl for each cell. For the cell with bright electrodes the ratio was 1.91417. For the one with platinized electrodes it was 1.91380. This shows a difference of about 0.02 per cent. or two parts in ten thousand in the two cells and a great part of this may well be due to experimental error, on account of poor temperature regulation, the poor sensitivity of the telephone at 2,000 cycles, error in plotting the curves, etc. From these and other similar measurements it would seem probable that the one inch platinized electrodes give the true resistance of the solution, and that we may be able to correct for the change in resistance with change in frequency with bright platinum electrodes, so that they can be used as well as platinized electrodes for making measurements of the conductivity of electrolytes, although perhaps with not so great an accuracy.

The work will now be continued under the direction of Dr. S. F. Acree at the University of Wisconsin.

NATIONAL BUREAU OF STANDARDS,
WASHINGTON, D. C.

A PROPOSED METHOD FOR THE PHOTOMETRY OF LIGHTS OF DIFFERENT COLORS.[1]

BY IRWIN G. PRIEST.

THE accompanying figure shows a horizontal plan of the proposed heterochromatic photometer. L_s and L_x are respectively the standard and the unknown lamp. L_c is the comparison lamp. L_c and L_s should be of the same color. S_1 and S_2 are opal glass screens. $L-B$ is a Lummer-Brodhun cube. O is the ocular focused on $L-B$. N is a fixed nicol prism. Q is a right-handed quartz plate cut perpendicular to the optic axis and placed

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 23–24, 1915.

with its optic axis coincident with the line of sight, ZZ. It is mounted so as to be readily removable from and replacable in the path of the light. The best thickness of Q is to be determined by trial. N' is a nicol prism which can be rotated about the axis ZZ. C is a divided circle by means of which the rotation of N' can be measured. (It may also be desirable to use a collimating lens between S_1 and N and a lens between N' and $L-B$ to image S_1 on the side of $L-B$ remote from O.)

The procedure of making a measurement is as follows:

Q is replaced by a colorless homogeneous and isotropic glass plate of about the same refractive index. N' is set at 90° from its previously determined position for total extinction. L_s and L_c are balanced by sliding L_s along XX, L_c having been set at a convenient standard position. L_s is replaced by L_x

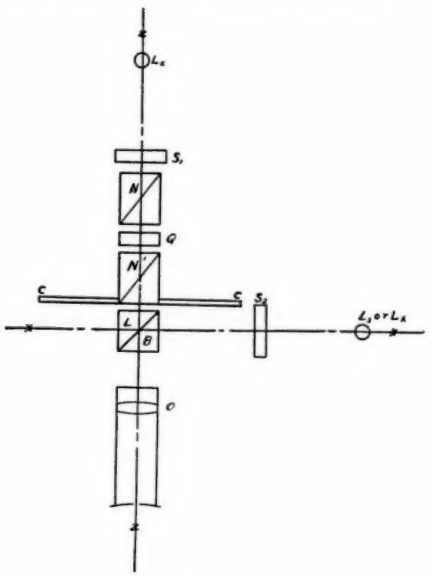

Fig. 1.

and Q is replaced in the path ZZ. By sliding L_c and at the same time turning N', a *complete match of both color and brightness* is obtained.

The candle power of L_x is computed as follows:

ϕ = angle through which N' was turned clockwise.

t = thickness of Q in millimeters.

T = transmission (ratio of emergent to incident light) of Q relative to the glass plate with which it is interchanged. (See above.)

R = ratio of brightness of S_1 when L_x is matched to its brightness when L_s is matched. (Determined by ordinary inverse square law.)

α_λ = specific rotation of quartz for light of wave-length λ.

V_λ = relative "visibility" of light of wave-length λ.

I_x = candle power of L_x.

I_s = candle power of L_s.

From ϕ, t, and the known rotatory dispersion of quartz compute the value of $V_\lambda \cos^2 (\phi - \alpha_\lambda t)$ for values of λ distributed through the visible spectrum. Plot $V_\lambda \cos^2 (\phi - \alpha_\lambda t)$ as a function of λ. Let S represent the ratio of the area of this curve to the area of the "visibility" curve.

I_x is given by

$$I_x = I_s \cdot R \cdot T \cdot S.$$

The computation can be very much simplified by the preparation of permanent tables showing $T \cdot S$ as a function of ϕ. Such tables should of course be based on the average of a large number of determinations of visibility, officially adopted as standard by consent of those interested.

This method has not been put into actual practice, but experiment[1] has demonstrated that, with such apparatus, using a quartz plate one millimeter thick, a perfect color match can be obtained between carbon and tungsten lamps, and that ϕ varies with the voltage on either lamp.

This idea is a "by-product" of other work the author is doing. Inasmuch as he is not in a position to have opportunity to put it into actual practice himself, he ventures to submit it to the consideration of others, without such detailed experimental work as would otherwise be considered necessary to precede its publication.

BUREAU OF STANDARDS,
WASHINGTON, D. C.

A NULL METHOD WITH PHOTO-ELECTRIC CELLS.[2]

BY F. K. RICHTMYER.

FOR certain laboratory purposes where light sensitive devices of extreme sensitivity are desirable, photo-electric cells of sodium or potassium offer exceptional possibilities. At present the use of such cells as are ordinarily obtainable on the market is somewhat limited by the so-called "dark current." Improvements in construction, by Ives and others, have largely eliminated this source of error. But even in such cells where the so-called dark current is large the following arrangement completely eliminates it while not in the least reducing the sensitivity. Further, this arrangement makes possible for certain kinds of work a precision of measurement not available in any other way.

e_1 and e_2 are sources of potential difference, which can be varied independently at will from 0 to 120 volts. The $-$ terminal of e_1 and the $+$ terminal of e_2 are connected, in a sort of Wheatstone's bridge arrangement, to the photo-electric cells c_1 and c_2 respectively. Points b and b' are connected by a sensitive Dolazelac electrometer, and are also grounded, b' through a suitable make and break key k.

[1] By use of the Arons Chromoscope. For description of this instrument see Ann. der Phy., 39, 545 (1912).

[2] Abstract of a paper presented at the Washington meeting of the Physical Society, April 23–24, 1915.

Relative values of e_1 and e_2 may by trial be so chosen that the dark current through c_1 shall be equal to that through c_2 as shown by the null reading of the electrometer when k is open. (This critical ratio e_1/e_2 seems to be somewhat variable for any pair of cells. It depends on conditions not yet fully studied.)

If now c_1 and c_2 be illuminated by sources L_1 and L_2 at distances d_1 and d_2, respectively, either d_1 or d_2 may be so adjusted *that the resultant photo-electric currents are equal*, as is again shown by the null reading of the electrometer. This adjustment may be made with a very high degree of precision, even with the simple cells obtainable on the market. One might call such an arrangement

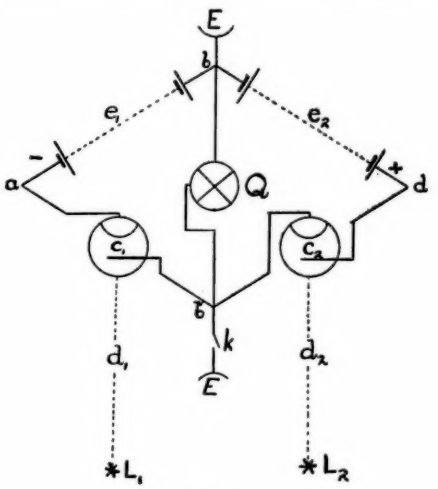

Fig. 1.

a "differential photo-electric photometer," since the sensitivity is limited only by the *absolute* difference (photo-electrically measured) in the two illuminations, and not by their relative difference, as is the case with visual photometers. In fact such an arrangement is to light measurements what the Wheatstone's bridge is to resistance measurements.

For various positions of L_1 there are corresponding positions of L_2 for a "balance." The following two sets of data give some idea as to the precision available.

If d_1 be plotted against d_2 a rigorously straight line results (not passing through the origin because in the particular apparatus used the positions of L_1 and L_2 were read on scales whose zero did not quite coincide with the sensitive surface).

These straight lines show that the two cells in question obey *exactly* the same current-illumination law, and further that this law must be a simple exponential one of the form

$$C = k \cdot I^x,$$

where C is the photo-electric current, I is the intensity of illumination, and x

L_1 and L_2 were 8 c.p. tungsten lamps.

Set 1. $e_1 = 28$ Volts, $e_2 = 36$ Volts.		Set 2. $e_1 = 47.2$ Volts, $e_2 = 52.8$ Volts.	
d_1	d_2	d_1	d_2
438.2 cm.	235.4	404.6	228.4
369.8	199.0	375.6	212.5
288.8	156.7	330.0	187.2
249.8	135.7	260.0	148.1
205.7	112.5	220.0	125.8
175.8	96.6	190.0	109.0
123.9	68.9	170.0	97.6
		155.0	89.3

is an exponent, which, according to previous observation is probably equal to unity. Indeed on the basis of the present experiment alone, it can hardly be anything else. Further work along this line is in progress.

There are many obvious applications of the above arrangement, particularly where small differences in illumination are to be measured or detected. The preliminary observations thus far made indicate that, so far as the photo-electric cells are concerned, differences in illumination of .01 per cent. are measurable. The sensitivity can be further increased many times by using more sensitive cells, better insulation, etc.

PHYSICAL LABORATORY,
CORNELL UNIVERSITY.

THE VISIBILITY OF RADIATION IN THE RED END OF THE VISIBLE SPECTRUM.[1]

BY EDWARD P. HYDE AND W. E. FORSYTHE.

THE visibility of radiation has been determined in a number of investigations among which may be mentioned particularly those of König,[2] Ives[3] and Nutting.[4] The two principal methods that have been employed are those of "equality of brightness," and "flicker," and the measurements have extended from 0.4 μ to 0.7 μ, though the data near these limits, as determined by Nutting, who has carried his measurements further than any other observer, are given only to one significant figure.

In connection with a problem in optical pyrometry recently investigated in this laboratory it was important to know the sensibility curve of the eye somewhat beyond 0.7 μ and to be certain of the values to a reasonable degree of accuracy. To this end the present investigation was undertaken, making use of an adaptation of the arrangement employed in the Holborn-Kurlbaum

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 23–24, 1915.

[2] König, Gesammelte Abhandlungen.

[3] Ives, Phil. Mag., Dec., 1912, p. 853.

[4] Nutting, Phil. Mag., Feb., 1915, p. 301. See also Bender, Ann. d. Phys., *45*, p. 115, 1914.

optical pyrometer. The advantage of the method of optical pyrometry lies in the availability of greater brightness, which permits the extension of measurements further toward the ends of the spectrum. Although, in accordance with our present needs measurements were confined to the red end of the spectrum, the method might be employed also in extending the sensibility curve in the short wave-lengths.

In Fig. 1 is shown the apparatus used. The spectrum of a broad vertical carbon filament (*A*) is formed by means of a Hilger constant deviation spectrometer in the focal plane of the telescope object-glass, in which plane is placed the horizontal filament of a second lamp (*F*). A lens (*H*) projects an image of this filament and of the background spectrum on a narrow vertical slit (*I*)

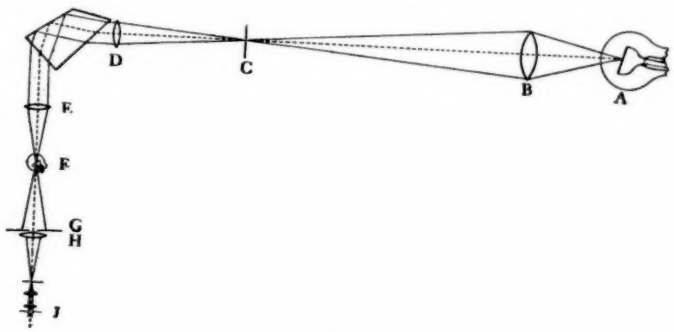

Fig. 1.

in the focus of the eye-piece (*J*). By rotating the drum-head of the spectrometer any spectral region may thus be brought into the field of view and compared in intensity with the pyrometer filament operated at a constant current. Rotating sectored disks placed between the carbon filament (*A*) and the colimator slit (*C*) of the spectrometer and quite close to the latter served to reduce the apparent brightness in the more luminous regions of the spectrum, the final settings being made by turning the drum-head of the spectrometer.

The energy curve of the broad-filament carbon lamp (*A*) was determined by comparison with a black body. In reducing the observed luminosities, corrections were made for dispersion, slit-widths, selective absorption of the lenses and prism, and scattered light. The illumination of the retina was well beyond the region of the Purkinje phenomenon, and the size of the field was extremely small, corresponding to a 2 mil filament magnified 6 times by the eye-piece.

Measurements made by 9 observers gave the average results shown in the accompanying table. In the second column are given the relative ordinates of the mean visibility curve of the 9 observers, taking the ordinate at $\lambda = 0.650\mu$ equal to unity. In the third, fourth and fifth columns are given the corresponding data of Nutting, Ives and König, as far as they overlap. The "equality of brightness" method was used in the determinations by

König and the "flicker" method by the other investigators. Our own data are given between the limits $\lambda = 0.630\,\mu$ and $\lambda = 0.770\,\mu$. It is quite practicable to extend the limit somewhat further into the red if there is any reason for it, and measurements might be made through the more luminous region of the spectrum and further into the blue than any previous measurements. It was, however, apart from our immediate purpose and hence was not undertaken.

The agreement between our values and those of the other investigators within the common region is as good as could be expected. The agreement among the different observers in our measurements in the red is probably better than that attainable in the more luminous region of the spectrum where the color differences are much more pronounced. It should be remembered that the agreement referred to pertains to the relative visibility in different wave-lengths of the red region rather than to the visibility in the red region compared with the visibility of white light, which was found to be markedly different for different observers.

Visibility Data on 9 Subjects in the Red End of the Spectrum.

Wave-lengths.	Mean Visibility of 9 Subjects.	Mean Values Given by Nutting.	Mean Values Given by Ives.	König's Values.
0.630	280	265	262	234
.640	170	160	168	164
.650	100	100	100	100
.660	53	54	65[1]	55
.670	27	30	42[1]	25
.680	13	13	25[1]	
.690	6.3	7.5		
.700	3.2	2.0		
.710	1.6			
.720	.79			
.730	.39			
.740	.19			
.750	$.09_5$			
.760	$.04_5$			
.770	$.02_0$			

[1] Extrapolated values.

THE EFFECTIVE WAVE-LENGTH OF TRANSMISSION OF RED PYROMETER GLASSES AND OTHER NOTES ON OPTICAL PYROMETRY.[1]

BY EDWARD P. HYDE, F. E. CADY AND W. E. FORSYTHE.

A. THE EFFECTIVE WAVE-LENGTH OF TRANSMISSION OF RED PYROMETER GLASSES.

IT is common practice to employ so-called monochromatic glasses in the eye-piece of an optical pyrometer. Among the glasses commonly used are Jena "Kupferrubin" glass No. F-2745 and Jena "Rotfilter" No. F-4512.

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 24, 1915.

The transmission of a specimen 2.9 mm. thick of what is supposed to be the "Rotfilter" glass is shown in curves (*a*) and (*a'*) in Fig. 1. The transmission of two thicknesses of the glass (5.8 mm.) in the visible spectrum is given by the curve (*b*). It is seen that the transmission band is rather broad, though the apparent breadth, as observed with a spectroscope, is much less owing to the limit of vision. It has been recognized by Waidner and Burgess,[1] Pirani[2] and others that, owing to the breadth of the transmission band, the effective wave-length of monochromatic light is subject to change with change in spectral distribution of the incident radiation, as occasioned by changes in temperature of the radiating source under investigation.

Attempts have been made to determine the effective wave-length of monochromatic light for various specimens of pyrometer glass by estimation of the wave-length of maximum luminosity in the prismatic spectrum of a source observed through the glass screen, and Waidner and Burgess[3] have attempted to show how this wave-length changes with a change in the temperature of the source used. This method of determining the effective wave-length is subject to criticism on two grounds. First, the wave-length of maximum luminosity determined in this way is not, in general, the center of gravity of the luminosity curve of transmission; and, secondly, the wave-length corresponding to the center of gravity in any region of temperature is not of particular significance, but rather that wave-length, such that for any definite temperature interval the ratio of the radiation intensities in that wave-length shall equal the ratio of the integral luminosities through the glass screen.

Various values of effective wave-length of monochromatic light for the red glass screens used with the Holborn-Kurlbaum pyrometer have been used, the determination of this wave-length having been made in the ways indicated above. A value as low as 0.658 μ has frequently been used. Moreover, Waidner and Burgess by their method outlined above, found that the effective wave-length seemed to become longer at higher temperatures,—a result quite contrary to expectation. Owing to the importance of knowing the effective wave-length in accurate measurements in pyrometry the present investigation was undertaken, using a double thickness (5.8 mm.) of the best, or most nearly monochromatic glass in our possession, viz., that for which the transmission curve is given in Fig. 1, and probably of the kind known as Jena "Rotfilter" No. F–4512.

It was desired to determine the effective wave-length between two definite temperatures of a black body, and to determine how this effective wave-length changes as the temperature interval is changed. Two methods were employed: (1) that of direct measurement; and (2) that of computation, assuming a knowledge of the visibility curve of the eye. An electric incandescent lamp at two arbitrary currents, corresponding in energy distribution to a black body at 1600° K. and at 2000° K. respectively, was selected as the source,

[1] Bull. Bur. of Stnd., *3*, p. 163, 1907.

[2] Verh. d. Deut. Phys. Ges., *15*, p. 826, 1913. See also ibid. *17*, p. 47, 1915.

[3] Loc. cit.

and the measurements were made using a double thickness of glass (5.8 mm.), as this thickness of glass is usually used.

By the first method, the ratios of emission intensities of the source for a number of wave-lengths at the two temperatures were measured, and these ratios compared with the ratio of integral luminosities of the radiation from the source observed through the double thickness of glass. These measurements were carried out with two distinct sets of apparatus. In one set of measurements the ratios of the radiation intensities were measured with a spectro-photometer, and the integral luminosities were determined with a Lummer-Brodhun photometer having the double thickness of red glass in the eye-piece. In the other set of measurements the ratios of the radiation intensities were determined with a spectral pyrometer, and the ratios of the integral luminosities were measured by the use of a laboratory form of the ordinary Holborn-Kurlbaum pyrometer having two thicknesses of the red glass in the eye-piece.

By the second method the integral luminosities through the red glass at the two chosen temperatures were computed from a knowledge of the spectral energy curves (computed from Wien's equation), the transmission curve for

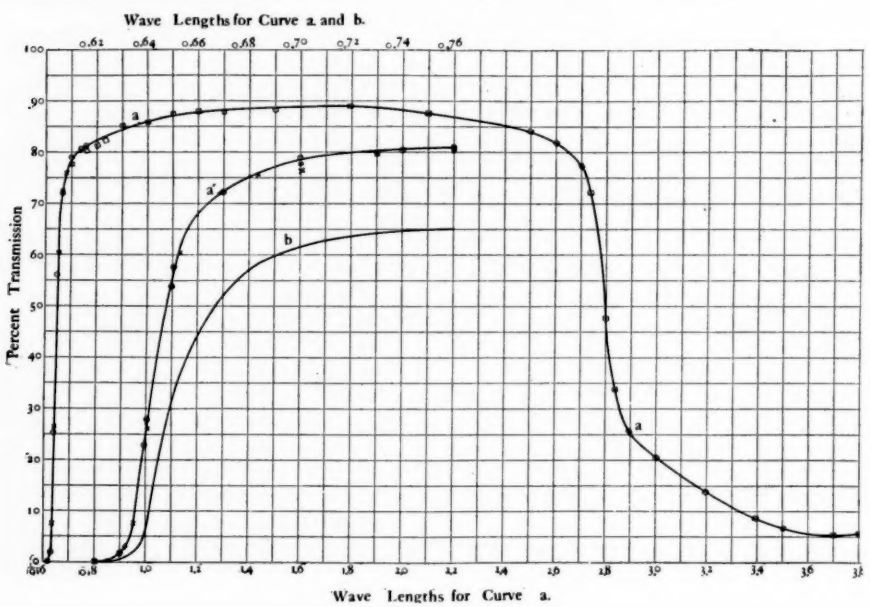

Fig. 1.

the glass (Fig. 1, curve (*b*)), and the sensibility curve of the eye. Inasmuch as the best published visibility data extend only to 0.7 μ and are only given to one significant figure in this region, which is most important in the present investigation, a preliminary investigation of the sensibility of the eye in this region was undertaken.[1] The data obtained in this preliminary investigation were used in the present computations.

[1] See previous abstract.

The results obtained by the two methods of direct experiment and by the method of computation are given in Table I.

TABLE I.

Effective Wave-Length of Monochromatic Transmission for Two Pieces of Red Pyrometer Glass, 5.8 mm. Total Thickness, Between the Temperatures 1600° K. and 2000° K.

Direct experiment, using spectrophotometer	$0.664\ \mu \pm 0.001\ \mu$
Direct experiment, using pyrometer	$0.663_5 \pm 0.001$
Computed value	0.663_8
Mean	$0.664\ \mu \pm 0.001\ \mu$

The next point of interest lies in the variation of this effective wave-length with change in temperature in the source studied. These variations can be determined most accurately by the method of computation, and as the changes in effective wave-length are small it is unnecessary to give the value for more than a few temperature intervals. In Table II. are given the results of these computations, assuming the effective wave-length between 1600° K. and 2000° K. to be the mean value given in Table I.

TABLE II.

Computed Changes in the Effective Wave-Length of Transmission of Two Thicknesses (5.8 mm.) of Red Pyrometer Glass for Various Temperature Intervals.

Temperature Interval.		Effective Wave-length.
1336° K.–1600° K.		$0.664_9\ \mu$
1600° – 1822°		0.664_1
1822° – 2400°		0.662_9
2400° – 3100°		0.661_7
1336° – 1822°	(Gold to palladium)	0.664_8
1336° – 3100°		0.663_4

Observations made on other pieces of glass used with the Holborn-Kurlbaum and other pyrometers indicate quite appreciable deviations from the particular specimen studied in the present investigation. As obviously it would be inconvenient to subject every sample of glass to such an investigation as recorded here, it appears desirable to find a simple way of calibrating glasses in terms of the specimen here investigated. This can be done readily, by determining the ratio of the apparent candle-power of a standard lamp at two definite currents, using the glass under investigation in the eye-piece of a Lummer-Brodhun or other suitable photometer, and comparing this observed ratio with the known ratio as determined with the known sample of glass in the eye-piece of the photometer. If the ratio with the test glass is found to be, say 1 per cent. greater than the given ratio for the standard glass, then the effective wave-length for the temperature interval corresponding to the two currents through the lamps must be shorter than the accepted wave-length of the standard glass by an amount readily computed from Wien's equation of spectral energy distribution, and from the known black body "color match" temperatures of the lamp at the two currents. Until the standardization of

glasses may be undertaken by the Bureau of Standards, Nela Research Laboratory will be glad for the convenience of other investigators to calibrate red glasses in terms of our standard, or else will, if desired, furnish at cost lamps calibrated between two definite currents, giving the black body "color match" temperatures and the ratio of apparent candle-powers as determined with the standard red glass in the eye-piece.

B. The Temperature Coefficient of Transmission of Red Pyrometer Glass.

In connection with the investigation described above it was observed that the transmission of the red pyrometer glass, presumably made with copper oxide, and dependent for its color on a colloidal solution, is subject to a large change with temperature. This has not been investigated thoroughly, but observations were made at two temperatures 20° C. and 81° C. by immersing

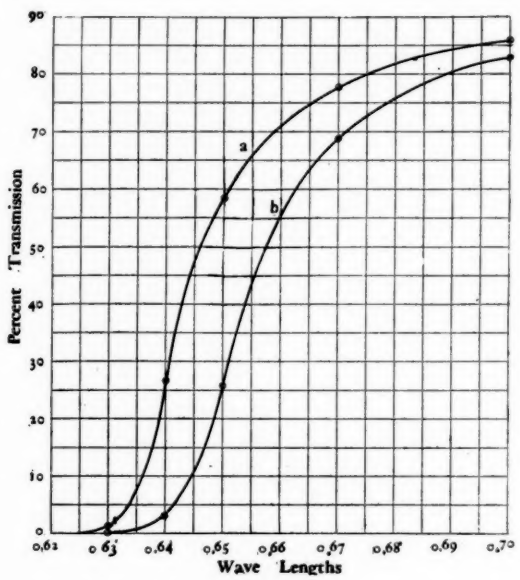

Fig. 2.

the glass in water heated to these two temperatures. The results are given in Fig. 2. Curve (*a*) is the transmission of the glass at the lower temperature 20° C., and curve (*b*) the corresponding curve at the higher temperature 81° C. The transmission is shown to decrease with increase in temperature, the coefficient of temperature change being greatest in the shorter wave-lengths. The change is such as to make the transmission band appear to shift to longer wave-lengths as the temperature is increased. A further investigation of this should give data with which to test the theoretical formula of Mie[1] for colloidal solutions.

[1] Ann. d. Phys., *25*, p. 377; 1908.

C. Influence of Position of Rotating Sectored Disk in Use with the Holborn-Kurlbaum Type of Pyrometer.

If a rotating sector is used with an optical pyrometer to reduce the intensity of the source, care must be taken as to the location of the sector. There is a very marked difference in the results of temperature measurements depending upon whether the sector is located near the projection lens or as near as possible to the pyrometer lamp. There is also a difference depending upon the relative position of the openings in the sector and the source providing the source consists of a lamp filament. If a sector of small transmission is mounted near the lens and so placed that the openings of the sector are parallel to the axis of the filament when passing across the center of the lens, the definition is very bad while if the openings of the sector are turned through 90° so that they are perpendicular to the axis of the filament, the definition is quite good. When the rotating sector is located near the pyrometer lamp the definition is good and independent of the position of the openings of the sector. If a very large source, as for example a black body, is used no such effect is to be noted.

If a lamp filament used as a background be set so that it has the same brightness as a black body at 1822° K. (the temperature of melting palladium) as determined by the optical pyrometer using red glass before the eye-piece and this background again set at the brightness corresponding to the melting point of gold as indicated by the black body, the relation between these two lamp brightnesses as determined by the rotating sector if placed near the projection lens is not the same as that for a black body over the same range. The differences are relatively small when the sectored disk is mounted near the pyrometer lamp.

NELA RESEARCH LABORATORY,
NATIONAL LAMP WORKS OF GENERAL ELECTRIC CO.,
NELA PARK, CLEVELAND, O.,
April, 1915.

ANEROID BAROMETERS.[1]

BY M. D. HERSEY.

A PRIMITIVE type of aneroid barometer was invented in 1798 to meet the needs of aeronautics at the time. The present activity in aviation has again directed attention to the difficulties involved in the accurate use of this instrument. The first aneroid was found to be worthless on account of temperature effects. It was forgotten, and in 1847 a successful aneroid was independently invented. This later aneroid did not have its vacuum box so completely exhausted; consequently, the expansion of the confined air with rising temperature just compensated for the diminishing stiffness of the metal.

The aneroids at present in use differ only in details from that of 1847. During the ten years following this date a number of new types of mechanism

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 23–24, 1915.

appeared, including the Bourdon aneroid (apparently the precursor of the Bourdon pressure gage), and the Goldschmid aneroid (which dispenses with the fragile lever system, readings being taken with a micrometer screw). Then, as contributions to the mechanical development of the aneroid fell off, the frequency of published articles on the accuracy of aneroids rapidly increased. A great many such articles appeared about 1880. These investigations would usually end by announcing that, under good conditions, the "probable error" of an aneroid is a certain number of hundredths of a millimeter.

About 1890 an important investigation by the late explorer, Edward Whymper, showed that errors of a thousand feet (some 20 millimeters on the pressure scale) might occur in the practical use of aneroids at high altitudes, owing to their inherent tendency to "creep" or drift in their indications when held at a constant low pressure. Chree, in 1898, published a statistical study of aneroid tests and experiments at Kew Observatory; expressing the numerical magnitude of this drifting effect, in its several manifestations, by empirical equations. But these interesting figures were not accompanied by a sufficient description of the mechanical details of the aneroids to enable us to trace the errors to their sources; in a word, he investigated the dependent, but not the independent variables of the problem. Immediately after this, Prof. C. F. Marvin, on the basis of certain experiments, urged the need of a physical study of the aneroid, and, in particular, of the vacuum box. Important additions to the available data are also to be found in the publications of the Physikalisch-Technische Reichsanstalt.

However, all this material is fragmentary, and, in itself, inadequate to answer the two questions confronting the Bureau of Standards, viz.: What specifications will insure the selection of a good aneroid for a particular purpose? and, How shall aneroids be tested in order to get corrections that are applicable in practical use? Consequently, four years ago, the Bureau undertook a general experimental study of the accuracy of aneroid barometers. Certificate blanks have recently been issued[1] containing a provisional set of specifications and method of testing. From time to time these will be revised.

In the course of the investigation the following points have been considered:

1. The coördination of existing data.
2. Recognition of the physically distinct uses to which aneroids are put.
3. Defects frequently met although readily avoidable.
4. The classification of errors and determination of characteristic curves showing their variation with conditions, viz.:

I. Transient errors: including effects of temperature lag, etc.

II. Inherent errors: including those due to looseness, friction, lack of balance, elastic after effect and hysteresis, thermal expansion, temperature change in elastic modulus and hysteresis, etc.

[1] The Bureau has also published a Circular (No. 46) on The Testing of Barometers. This circular, which is equally concerned with mercurial and aneroid barometers, is written for the guidance of persons who are already familiar with the use of such instruments and wish them standardized at the Bureau. A brief enumeration of the defects and errors to be guarded against is followed by a schedule of fees for the various tests.

III. Secular errors: including effects of pressure oscillations, of shocks received in transportation, and of age alone.

5. The localization of sources of error:

(*a*) Statistically, correlating errors with constructive details;

(*b*) Physically, isolating the parts and observing their separate action.

6. A comparative test of a number of representative aneroids to determine the degree of accuracy reasonably attainable.

7. Comparison of relative merits of diverse types of construction.

8. Comparison of results of different methods of testing; including a study of the seemingly contradictory reports furnished by the government laboratories of England, France, and Germany on two aneroids taken abroad in 1913.

9. Mathematics of the action of an ideal aneroid, *i. e.*, one conceived to be free from sources of error; a necessary preliminary to any discussion of improvements in design.

10. Possible errors of barometric altitude estimation due to wind, moisture, and temperature irregularities in the air column.

In conclusion, it appears that errors which might otherwise mount up to 5 or 10 per cent. can usually be kept down to 1 or 2 per cent. by the intelligent selection and use of an aneroid for a given purpose.

A METHOD OF MEASURING HEAT CONDUCTIVITIES.[1]

BY R. W. KING.

UNDER the *boundary conditions*

$$\theta(o, t) = \theta_1 + \theta_2 \cos \omega t,$$
$$\theta(\infty, t) = 0,$$

the solution of the differential equation expressing the linear flow of heat is

$$\theta = \theta_1 e^{-p_1 x} + \theta_2 e^{-p_2 x} \cos(\omega t - qx)$$

where

$$q = \sqrt{\frac{k}{2}} \sqrt{-\mu + \sqrt{\mu^2 + u^2}},$$

μ being the radiation constant per unit of length and k the thermal conductivity divided by the product of density and specific heat. Thus it is seen that the velocity of propagation of the impressed heat wave depends, among other things, upon ω and μ; and it is possible, by determining experimentally the velocities corresponding to ω_1, ω_2 in a rod for which μ remains constant, to eliminate μ and express k in terms of ω_1, ω_2, v_1, v_2, the density and specific heat.

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 23–24, 1915.

The experiment here indicated has been performed upon metal wires about 2.5 mm. in diameter and from 25 to 40 cm. in length, the first boundary condition being maintained by inserting one end of the wire in a small heating coil through which was caused to flow a current whose value is given by the expression

$$I = I_0 \left| \sin \frac{\omega}{2} t \right| ,$$

and the second boundary condition being maintained through radiation. The velocities of propagation were determined by noting the time lag between the motions of two short-period galvanometers connected with thermocouples, these couples being attached a few centimeters apart to the end of the wire at which heat is applied.

The materials thus far worked with have been copper and tin, and sample results are shown in the following table.

Copper.			Tin.		
Period in Seconds.	Time Lag in Seconds.	Conductivity in Absolute Units.	Period in Seconds.	Time Lag in Seconds.	Conductivity in Absolute Units.
130.7	11.77	.910	129.7	11.30	.1551
293.0	15.52		290.0	14.36	
129.3	12.12	.907	130.1	11.41	.1543
291.3	16.60		294.5	14.66	
129.8	12.26	.906	128.3	11.22	.1553
293.0	16.97		287.7	14.31	

By enclosing the test piece and heating coil in an electric furnace, the conductivity of copper at 360° C. was found to be 0.858.

The method would thus seem to permit of an extension to high and low temperature work, and measurements of this nature are soon to be attempted. Whether or not it can also be utilized in measurements upon poor conductors has not yet been determined.

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A THEORY OF ADSORPTION.[1]

BY IRVING LANGMUIR.

BRAGG has shown that the atoms of crystals are arranged according to a space lattice, the identity of the molecules being lost. The forces acting between the atoms are thus chemical forces. In the case of diamond, the tetravalent character of carbon is manifest from the structure, but in most cases the valency appears to be *divided* between several atoms. Thus in sodium chloride the single valency of the sodium atom is divided between six chlorine atoms. There is a close connection between this theory and Werner's theory of valence.

On the surface of a crystal there must be unbalanced forces, so that the atoms may be considered to be in an unsaturated state. This is thought to be the cause of adsorption. An adsorbed film thus consists of atoms (or molecules) of the adsorbed material chemically held by the atoms of the solid so as to form a continuation of the space lattice of the solid. The surface of a crystal is thus looked upon as a checkerboard containing a definite number of spaces, each space capable of holding one atom (or molecule) of the adsorbed substance.

The amount of material adsorbed depends upon a kinetic equilibrium between the rate of condensation and the rate of evaporation from the surface. Practically every molecule striking the surface condenses (independently of the temperature). The rate of evaporation depends on the temperature (Van't Hoff's equation) and is proportional to the *fraction* of the surface covered by the adsorbed material. Molecules striking a surface already covered also condense, but usually evaporate much more rapidly than from the first layer. Hence, except where the vapor is nearly saturated, the amount of material adsorbed on a *plane surface* rarely exceeds that contained in a layer one atom (or molecule) deep.

This theory is based on and seems to be in good accord (both qualitative and quantitative) with phenomena of:

1. Electron emission from heated metals.
2. Photoelectric effect.
3. Kinetics of heterogeneous chemical reaction (catalysis).
4. Electrochemical action, especially polarization and passivity.
5. Evaporation.
6. Heat conduction in gases at low pressures.
7. Adsorption.

Passivity.—According to this theory, a metal electrode in an aqueous solution is nearly completely covered with hydrogen and oxygen atoms (or OH radicals), chemically combined with the metal atoms, thus forming a layer one atom or molecule deep. In the case of metals such as platinum, the rate

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at which the oxygen atoms leave the surface (evaporate into the solution) is large, compared to the rate at which the hydrogen atoms evaporate, whereas with metals like iron and nickel the reverse is true. A layer of oxygen atoms renders the surface passive, while hydrogen renders it active. Hydrogen may destroy the oxygen layer and remove passivity.

This theory seems to combine the advantages of Faraday's oxide theory, Le Blanc's reaction velocity theory, Foerster and Schmidt's hydrogen activation theory, and Reichinstein's constant-sum theory (this latter because of the definite number of spaces available on the surface of the electrode).

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